



APTD -1106

PB 209 267

FINAL REPORT

IMPROVED CHEMICAL METHODS FOR SAMPLING AND ANALYSIS OF GASEOUS POLLUTANTS FROM THE COMBUSTION OF FOSSIL FUELS

VOLUME I
SULFUR OXIDES

Contract No. CPA 22-69-95

JUNE 1971

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Prepared for
ENVIRONMENTAL PROTECTION AGENCY
Cincinnati, Ohio

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BIBLIOGRAPHIC DATA SHEET		1. Report No. APTD-1106	2.	3. Recipient's Accession No.	
4. Title and Subtitle Improved Chemical Methods for Sampling and Analysis of Gaseous Pollutants from the Combustion of Fossil Fuels Volume I Sulfur Oxides			5. Report Date June 1971		
7. Author(s) J. N. Driscoll and A. W. Berger			8. Performing Organization Rept. No.		
9. Performing Organization Name and Address Walden Research Corporation 359 Allston Street Cambridge, Massachusetts			10. Project/Task/Work Unit No.		
			11. Contract/Grant No. CPA 22-69-95		
12. Sponsoring Organization Name and Address ENVIRONMENTAL PROTECTION AGENCY, Office of Air Programs Division of Control Systems, Process Measurements Section Cincinnati, Ohio			13. Type of Report & Period Covered Final		
			14.		
15. Supplementary Notes					
16. Abstracts State-of-the-art manual methods are reviewed for sampling and analysis of sulfur oxides. The determination of sulfur dioxide (10-3000 ppm) and sulfur trioxide (5-300 ppm) is reviewed for stationary fossil fuel combustion sources and for control equipment which may be installed to reduce the emissions from such sources.					
17. Key Words and Document Analysis. 17a. Descriptors Air pollution Sulfur oxides Combustion products Chemical analysis Gas sampling					
17b. Identifiers/Open-Ended Terms Sources					
17c. COSATI Field/Group 13B					
18. Availability Statement Unlimited			19. Security Class (This Report) UNCLASSIFIED		21. No. of Pages 271
			20. Security Class (This Page) UNCLASSIFIED		22. Price

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Prepared under
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by
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June 1971

Prepared for
Environmental Protection Agency
Cincinnati, Ohio

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FOREWORD

The compilation of information contained in this publication was performed pursuant to Contract No. CPA 22-69-95, Air Pollution Control Office, Environmental Protection Agency.

The information was compiled by Walden Research Corporation and their subcontractor, Arthur D. Little, during the period June 12, 1969 to September 11, 1970.

Volume I of this report examines state-of-the-art manual methods for sampling and analysis of sulfur oxides. The determination of sulfur dioxide (10-3000 ppm) and sulfur trioxide (5-300 ppm) is reviewed for stationary fossil fuel combustion sources and for control equipment which may be installed to reduce the emissions from such sources.

Volume II reviews methods for the determination of oxides of nitrogen in stationary fossil fuel combustion sources for the concentration range 5-2000 ppm for nitric oxide (NO), nitrogen dioxide (NO₂), and total oxides of nitrogen (NO + NO₂ or NO_x).

Volume III of this report examines state-of-the-art manual methods for sampling and analysis of carbon monoxide in stationary fossil fuel combustion sources for the concentration range 10-1000 ppm.

The major pollutants of interest in this study are sulfur and nitrogen oxides. The report subsequently includes a literature search, review of methodology and laboratory investigation on the most promising methods. Carbon monoxide, the minor pollutant, was limited to a literature search and review of methodology.

This report has been reviewed and approved.

Robert L Larkin

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TABLE OF CONTENTS

<u>Section</u>	<u>Title</u>	<u>Page</u>
1	Introduction	1
	1.1 National SO _x Emissions and Method Application Priorities	1
2	The Combustion Effluent Environment	5
	2.1 Introduction	5
	2.2 General	5
	2.3 Temperatures	7
	2.4 Moisture	10
	2.5 Particulate Matter	10
	2.6 Sulfur Compounds	11
	2.7 Other Gaseous Species	11
	2.8 Transients	12
3	Chemistry of Sulfur Oxides in Flue Gases	13
	3.1 Introduction	13
	3.2 Properties of SO ₂ and SO ₃	13
	3.2.1 Equilibrium Constants for Formation of SO ₂ and SO ₃ from the Elements	13
	3.2.2 The Vapor Pressure of SO ₃	15
	3.2.3 The SO ₃ -H ₂ O-H ₂ SO ₄ Equilibrium	15
	3.3 The Oxidation of Gaseous SO ₂	15
	3.3.1 Homogeneous Oxidation	15
	3.3.2 Heterogeneous Oxidation	19
	3.3.3 Sulfate Decomposition	19
	3.4 Adsorption of SO ₂	21
	3.5 Solution Chemistry of SO ₂	21
	3.5.1 The Solubility of SO ₂	21
	3.5.2 Acid Dissociation Constants	25
	3.5.3 Redox Chemistry	25
	3.6 Conclusions	26
4	Manual Sampling Methods for Gaseous Pollutants ...	28
	4.1 Introduction	28
	4.2 Common Factors	28
	4.2.1 Pre-Test Planning	28
	4.2.2 Stack Measurements	29

TABLE OF CONTENTS (Cont.)

<u>Section</u>	<u>Title</u>	<u>Page</u>
4.2.3	Sampling Train Components	30
4.2.3.1	General	30
4.2.3.2	Evaluation of Specific Components	36
4.2.4	Representative Stack Sampling for Gases	40
4.2.5	Sampling Errors in Ducts	42
4.2.6	Variance of Concentration in Large Ducts	44
4.3	Flue Gas Flow Measurement Methods	47
4.3.1	Introduction	47
4.3.2	Pitot Tube Traverse	50
4.3.2.1	Velocity Measurements	52
4.3.2.2	Traverse	55
4.3.2.2.1	Equal Area Division of Ducts of Circular Cross Section .	56
4.3.2.2.2	Equal Area Division of Ducts of Rectangular Cross Section	58
4.3.2.2.3	Flow Variations During Traverse ...	61
4.3.2.3	Calculations of Volumetric Flow From Velocity Pressure	62
4.3.3	Low Velocity Flow Measurement	63
4.3.3.1	Micromanometer - Pitot Tube ..	63
4.3.3.2	Electronic Micromanometers ...	63
4.3.3.3	Hot-Wire Anemometer	65
4.3.3.4	Vane Anemometers	65
4.3.3.5	Plate Orifice Meter	66
4.3.4	Comparison of Volumetric Flow Measuring Methods	68
4.3.5	Indirect Determinations of Volumetric Flow	68
4.3.5.1	Stoichiometric Method	68
4.3.5.2	Dilution Technique	68

TABLE OF CONTENTS (Cont.)

<u>Section</u>	<u>Title</u>	<u>Page</u>
5	Sampling Methods for Sulfur Oxides	71
5.1	Introduction	71
5.2	Probes	71
5.2.1	Simple Probes	72
5.2.2	Temperature Controlled Probes	74
5.2.2.1	Heated	74
5.2.2.2	Water-Cooled	74
5.3	Collection Methods for SO ₃	74
5.3.1	Introduction	74
5.3.2	Absorption in a Liquid	78
5.3.2.1	80% Isopropanol	78
5.3.2.2	Boiling Water	87
5.3.2.3	Aqueous Sodium Hydroxide	87
5.3.2.4	Distilled Water	89
5.3.3	Condensation Methods	89
5.3.3.1	Controlled Condensation	91
5.3.3.2	Uncontrolled Condensation	94
5.3.3.3	Dewpoint Method	94
5.4	Collection Methods for SO ₂	95
5.4.1	Introduction	95
5.4.2	Aqueous Absorbents	96
5.4.2.1	Hydrogen Peroxide	96
5.4.2.2	Sodium Hydroxide	97
5.4.2.3	Iodine	99
5.4.2.4	Sodium Tetrachloromercurate	101
5.4.2.5	Stannous Chloride	103
5.4.2.6	Sodium Acetate	104
5.4.2.7	Collection Efficiency of Aqueous Scrubbers	105
5.4.3	Solid Adsorbents	112
5.4.3.1	Silica Gel	112
5.4.3.2	Adsorption on Molecular Sieve or Ion-Exchange Resins	116
5.4.3.3	Reactive Solid Sorbents	118
5.4.4	Dilution Methods	125

TABLE OF CONTENTS (Cont.)

<u>Section</u>	<u>Title</u>	<u>Page</u>
5.5	Comparison of Analytical Methods	126
5.5.1	Introduction	126
5.5.2	Analytical Methods for the Determination of Sulfate Ion or Sulfuric Acid	127
5.5.2.1	Titration with Barium Ion and Selected Indicators	127
5.5.2.2	Titration with Barium Ion Using Other Substituted Naphthalene Disulfonic Acid Derivatives ...	128
5.5.2.3	Titration with NaOH	130
5.5.2.4	Colorimetry Using Barium Chloranilate	131
5.5.2.5	Turbidimetry	132
5.5.2.6	Conductivity	133
5.5.2.7	Precipitation Reactions	134
5.5.2.8	Titration Involving Ethylenediaminetetraacetic Acid	135
5.5.2.9	Summary and Conclusions	136
5.5.3	Analytical Methods for the Measurement of Sulfite Ion Concentration	137
5.5.3.1	Iodine Titration by Decolorization of a Standard Iodine Solution	137
5.5.3.2	Iodine Titration of NaHSO ₃ Solution	137
5.5.3.3	West-Gaeke Colorimetric Determination of SO ₂	138
5.5.3.4	Acid Titration - NaHSO ₃ Solution	139
5.5.3.5	Conclusion	139
5.5.4	Laboratory Investigation of Analytical Methods for Determination of Sulfate Ion	140
5.5.4.1	Titration of Sulfate Solutions with Barium Perchlorate	140
5.5.4.2	Determination of Sulfate by the Barium Chloranilate Method	145
6	Statistics of Field Sampling and Analysis	154
6.1	Introduction	154

TABLE OF CONTENTS (Cont.)

<u>Section</u>	<u>Title</u>	<u>Page</u>
	6.1.1 Accuracy	154
	6.1.2 Precision	155
	6.2 Precision Obtainable in Field Sampling of Sulfur Oxides	155
	6.3 Comparison of Sampling Errors and Analytical Errors in the Determination of Sulfur Oxides	162
	6.4 Comparison of Stoichiometric to Measured SO ₂ Field Results	164
	6.5 Conclusions	165
7	Recommended Methods	168
	7.1 Collection Methods for SO ₃	168
	7.2 Collection Methods for SO ₂	169
	7.3 Analytical Methods	170
	7.4 Simplified Methods	170
	7.5 Correlation of Combustion Source Type with Selection of Sampling and Analysis Techniques	171
	Literature Cited	174
Appendix 1	Reference Data on the Combustion Effluent Environment	189
Appendix 2	Literature Search	211
Appendix 3	Discussion and Additional Studies of the Barium Chloranilate Method for Sulfate	215
Appendix 4	Sampling System for SO _x and NO _x	221
Appendix 5	Laboratory Dilution Systems	229
Appendix 6	Bibliography for Hydrogen Sulfide	235

LIST OF ILLUSTRATIONS

<u>Figure No.</u>	<u>Caption</u>	<u>Page</u>
2-1	Schematic of Stationary Combustion Systems	6
3-1	Equilibrium Constants for Formation of Sulfur Oxides	14
3-2	Equilibrium Concentrations of SO_2 and SO_3 vs. Temperature at Atmospheric Pressure	16
3-3	The Vapor Pressure of SO_3	17
3-4	The $\text{H}_2\text{SO}_4 = \text{H}_2\text{O} + \text{SO}_3$ Equilibrium	18
3-5	The Equilibrium Constant for the Reaction (1) vs. Temperature	20
3-6	Fraction of Total SO_x ... Oxidized to SO_3	20
3-7	Adsorption of SO_2 on Silica Gel	23
4-1	Observed Variations of Flow in Ducts	31
4-2	Sampling System Components	32
4-3	Probability of Obtaining an Accuracy within 15% of 9 Point Analysis for O_2 in a Large Duct	43
4-4	Schematic of Large Combustion Unit	45
4-5	Normalized CO_2 Traverse Data at Dust Collector of Coal-Fired Plants	46
4-6	A Standard Pitot-Static Tube	51
4-7	Effect of Yaw on Pitot-Static Combinations	54
4-8	Staubscheibe Pitot Tube	55
4-9	Calibration Factors, K, for Staubscheibe Pitot Tube .	55
4-10	Tangential Method for Duct Division	57
4-11	Types of Asymmetric Velocity Distribution in Pipes ..	59
4-12	Traverse Plan for Rectangular Duct	61
4-13	NACA Micromanometer	64
4-14	Vane Anemometers	66
5-1	Sulfuric Acid Dewpoint as a Function of SO_3 Concentration	73
5-2	Heated and Cooled Probes	75
5-3	Collection Devices for SO_3	80
5-4	Efficiency of SO_3 Collection	86
5-5	Collection Efficiency of Midget Impingers	88
5-6	SO_3 Controlled Condensation Apparatus	92
5-7	Acid Deposition Probe	95

LIST OF ILLUSTRATIONS (Cont.)

<u>Figure No.</u>	<u>Caption</u>	<u>Page</u>
5-8	Scrubber Configurations	106
5-9	Collection Efficiency of a Single Midget Impinger for SO ₂	111
5-10	Comparison of Detector Tube and Peroxide Collection Analysis for SO ₂	115
6-1	Measured SO ₂ (PHS-Shell Method), ppm	166
A4-1	Probe Module	222
A4-2	Collector Module	224
A4-3	Control Module	225
A5-1	Simple Dilution System for High Concentrations of SO ₂ and NO	230
A5-2	Dilution System	231
A5-3	SO ₃ Delivery System	232

LIST OF TABLES

<u>Table No.</u>	<u>Title</u>	<u>Page</u>
1-1	Nationwide Emissions of SO ₂ , 1966	2
1-2	Nationwide Emissions of SO ₂ , 1967	3
2-1	Size Categories for Stationary Combustion Sources ...	6
2-2	Emission Parameters for Fossil Fuel Combustion	8
2-3	SO _x Control Systems	9
3-1	Adsorption of SO ₂ on Carbon Black	22
3-2	Solubility of SO ₂	24
3-3	Acid Dissociation Constants	25
4-1	Comparison of Satisfactory Gas Meters for SO _x Sampling	38
4-2	Observed Coefficient of Variation for CO ₂ Traverse at Various Sampling Locations	48
4-3	Observed Coefficient of Variation for CO ₂ Traverse for Various Plant Types	49
4-4	Pitot Static Factors at Low Air Speeds	53
4-5	Location of Measuring Points for Log-Linear Method ..	58
4-6	Test Points for Rectangular Ducts	60
4-7	Diameter Ratios for Vane Anemometers	67
4-8	Comparison of Volumetric Flow Measuring Methods	69
5-1	Typical Power Plant Sampling Points	72
5-2	Comparative Summary of Sampling Devices	77
5-3	Collection Efficiency of SO ₃ in 80% IPA	79
5-4	Collection Efficiency of Midget Impingers for SO ₃ ...	82
5-5	Collection Efficiency of Midget Bubblers for SO ₃	84
5-6	Collection Efficiency of Lamp Sulfur Absorber for SO ₃	85
5-7	Comparison of SO ₃ Analyses as a Function of Collection Method	90
5-8	SO ₃ Collection Efficiency Using Controlled Condensation	93
5-9	Efficiencies of Absorbing Devices and Reagents for SO ₂	107
5-10	Collection Efficiencies of Single Midget Impingers for SO ₂	109
5-11	Collection Efficiency of Midget Impingers for SO ₂ in Peroxide	110

LIST OF TABLES (Cont.)

<u>Table No.</u>	<u>Title</u>	<u>Page</u>
5-12	Comparison of Detector Tube to Peroxide Impinger Collection for SO ₂	114
5-13	Standard Metal Compound Reaction Classes	119
5-14	Potential SO ₂ "Analytical" Sorbents at 400°K	121
5-15	Collection Efficiency of Solid PbO ₂ for SO ₂	124
5-16	Comparison of Collection Efficiencies of Solid Sorb- ents for SO ₂	125
6-1	Precision Statistics for SO ₃ by Controlled Condensa- tion	158
6-2	Precision Statistics for SO ₂ by Peroxide Collection .	158
6-3	BSI Sulfur Oxide Statistics	160
6-4	Comparison of Analytical Methods for SO ₂ After Caus- tic Absorption	161
A2-1	Primary Literature Sources Utilized in the Program ..	212
A2-2	Bibliographies	213

ACKNOWLEDGMENTS

We are pleased to acknowledge the assistance of Robert L. Larkin, the project leader for NAPCA. We thank Mr. Larkin and James Dorsey for sharing their experience with the project staff. We are indebted to Matt Stengel and Jim Martin of Combustion Engineering and John F. Smith of the Bureau of Mines for making available unpublished flue gas analysis data. We thank the following for their active interest and cooperation:

D. Barnhardt and J. Moore	Babcock and Wilcox
H. Chapman	Bethlehem Steel
E. Diehl and R. Young	Bituminous Coal Res.
F. Gottlich	Boston Edison
J. Hultz, H. Lang, W. O'Neil	Bureau of Mines
A. Plumley, W. Taylor	Combustion Engineering
J. Percival	Esso Res. & Engineering
R. Stevens, W. Smith	NAPCA-Durham
F. Gartrell	Tennessee Valley Authority

We thank Professors Paul Giever (Univ. of Michigan) and Melvin First (Harvard Univ.) and Alfred Thompson of Riley Stoker Corp. for valuable consultations. We also thank Mr. Cirvillo of Air Pollution Technical Information Center for the literature search conducted at our request.

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1. INTRODUCTION

This is Volume I of three volumes of the Final Report on "Improved Chemical Methods for Sampling and Analysis of Gaseous Pollutants from the Combustion of Fossil Fuels (in Stationary Sources)." The three volumes are divided by subject as follows:

- I Sulfur Oxides
- II Nitrogen Oxides
- III Carbon Monoxide

This report was prepared under Contract No. CPA 22-69-95 covering the period June 12, 1969 to September 11, 1970. The principal objectives of this program were: (1) to review the state-of-the-art methods for manual (wet chemical) methods for the determination of emissions of specified gaseous pollutants from (indirect-fired) stationary fossil fuel sources, (2) to select and develop improved procedures for high precision emissions determinations, and (3) to select and develop simplified procedures where high precision determinations were judged to be complex (i.e., required a highly trained research and development group).

The determination of sulfur dioxide (10-3000 ppm) and sulfur trioxide (5 to 10-300 ppm in the gas phase under stack conditions) is reviewed for effluent (or stream) temperatures up to ca. 900°F for stationary fossil fuel combustion sources and for control equipment which may be installed for such sources. Laboratory studies of the most promising methods are also included.

Since the practical utility of an analytical method is limited by the fundamental problem of obtaining a representative sample, we have necessarily included a discussion of the principles of flue sampling and the limitations so introduced to the overall accuracy and precision of a given determination.

In the following subsections, we consider method development priorities based upon national SO_x emissions, summarize the state-of-the-art in manual determination of sulfur oxides, and describe laboratory studies of the barium chloranilate and barium ion-thorin titration procedures.

1.1 National SO_x Emissions and Method Application Priorities

A rough guide to method development priorities may be obtained from the relative contributions of various sources to national SO_x emissions (Table 1-1).

TABLE 1-1
NATIONWIDE EMISSIONS OF SO_x, 1966 (521)*

		10 ⁶ tons/year
Total from Fossil Fuel Combustion in Stationary Sources		22.1
By Fuel	Coal	18.3
	Residual Fuel Oil	3.3
	Distillate Fuel Oil	0.5
By Sector	Power Generation ^a	14.0
	Industrial	5.6
	Residential and Commercial Heating	2.5

^aAbout 90% of the power generation contribution to SO_x emission is derived from coal-fired units and about 10% from oil (522).

Since SO_x emissions are primarily fuel dependent (518) rather than equipment dependent, the data of Table 1-1 essentially integrate the product of fuel use by sulfur content of the fuel. The above do not, however, distinguish fossil fuel effluents mixed with process emissions.

A somewhat more detailed breakdown, which excludes (direct-fired) process emissions, is available from work conducted at Walden (480), and is given in Table 1-2.

As may be seen from the Boiler Category of Table 1-2, 90% of total (non-process) emissions are attributable to watertube boilers, for which the smallest size range is about 25,000 pounds of steam per

* Literature references are listed at the end of the report.

TABLE 1-2
NATIONWIDE EMISSIONS OF SO₂, 1967
(Excluding Process Emissions)* (480)

	10 ⁶ tons/year
Total from Fossil Fuel Combustion in Stationary Sources	18.63
By Fuel	
Coal	15.60
Residual Fuel Oil	2.76
Distillate Fuel Oil	.27
By Sector	
Utilities	12.58
Industrial	4.28
Commercial	1.53
Residential	.24
By Boiler Category (excluding residential)	
Watertube ≥500,000 pph	9.29
Watertube ≤500,000 pph	6.50
Firetube	.88
Cast Iron	.72

*Also excludes stationary turbines and reciprocating internal combustion stationary engines.

hour (or ca. 3×10^7 Btu/hr). The SO_2 emissions determination problem is centered in these relatively large sources. Further examination of the categories of Tables 1-1 and 1-2 reveals that the highest priority is clearly to be placed upon analytical methods and equipment applicable to large boilers, both as the largest sources, and in consequence of the probable first application of control techniques to these sources.

It does not appear desirable to develop specially adapted high precision methods applicable to the myriad and relatively unimportant small sources at this time.

In the following section, we describe the effluent compositions from fossil fuel fired stationary combustion sources. The emphasis is upon those factors which influence the selection of sampling and analytical methods for sulfur oxides.

2. THE COMBUSTION EFFLUENT ENVIRONMENT

2.1 Introduction

A prerequisite for the selection of manual chemical methods for sampling and analysis of gaseous pollutants from the combustion of fossil fuels is the description of the environments to be sampled. The combustion products from all stationary sources such as steam generators, process heaters, water heaters and air (space) heaters are to be considered, except for those cases where process emissions are combined with the combustion products, e.g., a lime kiln or blast furnace. The measurements will normally be required at stack conditions; however, they may also include conditions at the inlet and outlet of sulfur oxides control equipment.

2.2 General

All combustion equipment can be generalized in terms of the schematic shown in Figure 2-1. Fuel is burned in a furnace to release heat. Combustion products and ash are generated as undesirable by-products. The combustion heat is transferred in a heat exchanger to some convenient thermal fluid, usually water, steam or air. Domestic heaters are familiar, simple examples of this generalized system. They are designed to provide unattended service over long periods of time to untrained users. Consequently, they are characterized by a low level of sophistication in combustion control, heat transfer (thermal efficiency) or air pollution control. On the other end of the sophistication spectrum are the new steam generating units at power plants. While the generalized combustion system shown in Figure 2-1 is still applicable, it is embellished considerably by combustion air pre-heaters, economizers, high pressure heat exchangers and pollution control equipment. In addition, computerized systems are utilized to monitor and control furnace and heat exchanger operation. The combustion products may be modified by the use of additives, either in the fuel, or added in the furnace or heat exchangers.

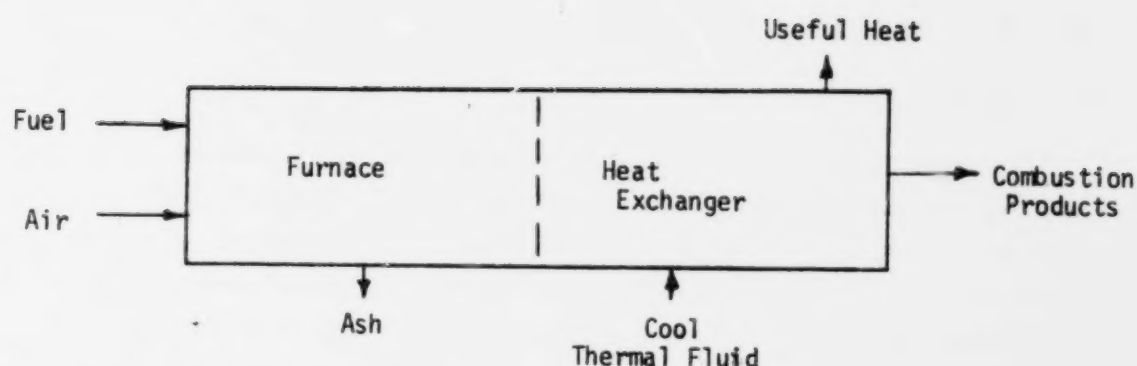


Figure 2-1. Schematic of Stationary Combustion Systems

For this evaluation, we have divided combustion equipment into three arbitrary size groups as shown in Table 2-1 in several approximately equivalent ways. There are relatively few suppliers of equipment in the large size range (4 major sources) with 1968 annual sales

TABLE 2-1
SIZE CATEGORIES FOR STATIONARY COMBUSTION SOURCES

	Large	Intermediate	Small
BTU Per Hour	$\geq 5 \times 10^8$	$3 \times 10^5 - 5 \times 10^8$	$< 3 \times 10^5$
Boiler Horsepower	$\geq 15,000$	10-15,000	< 10
Pounds of Steam Per Hour	$\geq 500,000$	350-500,000	< 330
Megawatts	≥ 50	$< 50 \text{ MW}$	Not Applicable

of the order of 75 units (556). On the other hand, there are several hundred suppliers of small units with 1967 annual shipments of approximately 1,500,000 units (557). Useful life is perhaps 15 and 30 years, respectively, for the small and large units. Combining the large number of installed units with the disparate designs, range of fuels used, load factors, varying operating practices, etc., it is clear

that it is totally impractical to attempt to specify the environment for individual cases. Rather, we have reviewed the range of environments reported in the literature for each of the three size categories shown in Table 2-1 for oil, coal and gas. A summary of emission parameters is given in Table 2-2 in consistent units ($\#/10^6$ BTU). Details are given in Appendix 1. A summary of conditions before and after control equipment for the most prominent SO_x control systems is given in Table 2-3. From these data the various requirements for principal factors such as required sensitivity, possible interferences, transients and temperature regimes may be determined. The major factors are briefly described below.

2.3 Temperatures

Sampling equipment must be designed to tolerate "normal" operation as well as unusual temperature excursions. In general, large units are designed for stack temperatures of 300-400°F. Gas-fired unit emissions, as a result of their freedom from the effects of corrosive sulfuric acid mist, run cooler, about 275°F. In domestic units stack temperatures are much higher, to 700-800°F. Inlet temperatures of the Monsanto SO_x control process also run at this level. Intermediate combustion units cover the range of temperatures between these extremes (400-700°F).

The implications of this temperature variation for sampling are four-fold:

1. Materials of construction must be adequate to tolerate the highest temperature.
2. Materials must be chosen to eliminate high temperature catalytic oxidation of SO_2 to SO_3 in the sample probe and lines.
3. Water and acid condensation must be taken into consideration in design of the sampling train. The sample stream should be kept hot insofar as possible, up to the collection equipment.

TABLE 2-2
EMISSION PARAMETERS FOR FOSSIL FUEL COMBUSTION^a (pounds/10⁶ BTU)

	GAS ^b		OIL ^c		COAL ^d	
	Large	Intermed. Small	Large (Resid.)	Intermed. (Resid./Dist.) Small (Dist.)	Large	Intermed. Small
Velocity ft/min	2000-3000		2000-3000		2000-3000	
Moisture	-----	18% @ 0% XS Air 15% @ 20% XS Air -----	-----	10% @ 0% XS Air 9% @ 20% XS Air -----	-----	6% (Nominal) -----
Excess Air %	15	15-75	20	20-75	25	25-75
Stack Temp. °F (of Breeching)	275-400	400-750	300-400	400-750	300-400	400-750
CO	Neg.	4x10 ⁻⁴	3x10 ⁻⁴	0.01/0.01	0.02	0.1-2
SO ₂	4x10 ⁻⁴	4x10 ⁻⁴	1.65	1.65/0.31	3.5	3.5
SO ₃			0.03	0.016/3x10 ⁻³		
NO						
NO ₂	0.35	0.2	0.68	0.47/0.51	0.8	0.8-0.3
Particulate	0.014	0.016	0.07	0.15/0.10	0.46	0.53
Hydrocarbons	Neg.	Neg.	0.022	0.01/0.01	(90% cont.) (65% cont.)	0.8 (uncont.)
Transients	10% of Capacity Per Min.		10% of Capacity Per Min.		8x10 ⁻³	0.04-0.4
					5% Capacity Per Min.	

- a. Details in Appendix 1, Final Report, Vol. I c. Sdist. 0.39%, 142,000 BTU/Gal
b. 1100 BTU/SCF Sresid. 1.6%, 152,000 BTU/Gal
d. S = 2.5%, 8% ash, 13,000 RTU/#

TABLE 2-3
SO_x CONTROL SYSTEMS (553)

Developer	Process	BEFORE		Temp. °F	Input	Temp. °F	AFTER		SO _x *
		Temp. °F	Temp. °F				Output	Output	
CE	Wet Scrubbing (Dolomite)	250-300	250-300	250-300	Normal Double Load Particulates	250-300	99% Particulate Removal	99% Particulate Removal	SO ₂ -99% Re-moved SO ₂ -90% Re-moved
Monsanto	CAT-OX	850	850	250	Follows 99% + Elect. Precip.	250	--	--	(Same)
Bumines	Alkalized Alumina	625	625	250	Recommend 3 0.9 gr/ft ³	250	Follows Cyclone Separator	Follows Cyclone Separator	(Same)
Reinluft	Char. Absorption	250-300	250-300	250	Recommend 3 0.9 gr/ft ³	250	--	--	(Same)
Wellman-Lord	Alkali-Sulfite Absorption	300	300	250	Only as Req'd by Power Plant Equipment	250	+95% Particulate Removal by Special Scrubber	+95% Particulate Removal by Special Scrubber	(Same)
TVA	Dry Dolomite Absorption (Intermittent)	Additive Rate of 2 Times Stoichiometric Requirement	Additive Rate of 2 Times Stoichiometric Requirement	250-300	2-3 times Particulate Load in Flue Gas Stream and Bottom Ash	250-300	25-50% SO ₂ 99% SO ₃	25-50% SO ₂ 99% SO ₃	25-50% SO ₂ 99% SO ₃

* Design Efficiencies Assumed

4. Hot probes and hot stacks make for uncomfortable working conditions requiring asbestos gloves. Severe manipulative constraints are imposed in handling of delicate apparatus, small connectors, etc. which should, therefore, be avoided.

2.4 Moisture

Combustion effluents possess a high moisture content which introduces a number of problems.

1. Uncontrolled condensation losses in sample lines may lead to losses of soluble species (SO_2 , SO_3).

2. Uncontrolled condensation in the sampler may lead to dilution of reagents.

3. Uncontrolled condensation can confuse the determination of water content of the stack gases. Determination of water is required whether results are reported on a "dry gas" basis or at "stack conditions".

4. Sample train components must not corrode in the high moisture/acid environment.

2.5 Particulate Matter

The objective of the methods under discussion is to determine gaseous contaminants. However, particulate matter can be an impediment and should be removed from the sample stream prior to the collection of gaseous SO_2 and SO_3 for several reasons.

1. Material adsorbed on particles will falsify the results.

2. Fly ash can catalyze the oxidation of SO_2 to SO_3 [even in dilute solutions, (527)], thereby distorting the true conditions.

3. Acid mist should be quantitatively removed from a sample stream if one is to determine gaseous SO_3 . Heated sampling lines are then used to prevent further condensation of gaseous SO_3 .

The uncertainty involved in collecting SO_3 mist and not re-evaporating it is great in a heated sampling system. Consequently, the preferred method is to remove the acid mist in a prefilter heated well above the dewpoint and to maintain such a temperature through sampling lines to the collector.

Obviously, the determination of SO_3 associated with fly ash or soot is ambiguous using this procedure and contributes to the confusion in SO_3 values reported in the literature. Particulate matter interference with SO_3 determination in the important large coal-fired units may be a very serious problem because of the high particulate loading.

Particulate matter from residual and distillate oil-firing is substantially smaller. Although the sulfur content of the residual oils can be significant, the analysis problem is less severe than that for coal. Particulate emissions from gas fired units are very low, as is sulfur content of the effluent gases.

2.6 Sulfur Compounds

Sulfur compound emissions are insignificant for most gas-fired units but substantial for oil and coal. Sulfur compounds in the combustion effluent from coal are ca 10^4 higher than for comparable gas-fired units. The chemistry of the sulfur compounds in flue gases is discussed in Section 3. Typical values and their ranges for the major fuels are discussed in detail in Section 6.

2.7 Other Gaseous Species

Other gaseous species, both major (CO_2 , O_2) and minor (NO_x , CO , HCl , etc.) are of interest, here, specifically as possible interferences in methods for the determination of sulfur compounds. Since these effects are specific, they are discussed in detail in Section 5 for each method considered.

2.8 Transients

Description of a transient requires the ability to sample for several short intervals over the duration of the transient. Transients related to load changes can be expected to vary from 1 or 2 minutes to approximately 30 minutes. For convenience, power plants will usually go from no to full-load in about one-half hour and will make smaller load changes (say, 100 → 70%) over about 15 minutes. However, new boilers are designed for fast load changes with gas and oil-fired units capable of 10% of full capacity per minute [10 minutes to full load (555)]. Because of greater difficulty in fuel transfer, metering and valving, coal-fired units can only be designed for about one half this load change rate (20 minutes to full load).

Domestic oil-fired units generally do not modulate the fuel flow but go from "off" to "on". Steady state combustion based upon soot emission takes about 10 minutes (512). This period is precisely the average "on" time for a domestic oil furnace (512). Consequently, domestic units are essentially always operating in a transient mode.

Manual methods for sulfur compounds described in the following are best suited for continuous sampling and are, therefore, averaging techniques of limited time resolution. Although it is certainly feasible to increase sampling rates to increase time resolution, say to the order of five minutes, transients are clearly best described by fast response instrumental methods.

3. CHEMISTRY OF SULFUR OXIDES IN FLUE GASES

3.1 Introduction

Sulfur, contained as an impurity in fuel, is converted nearly quantitatively, during the combustion process, into the two stable oxides of sulfur, SO_2 and SO_3 . About 98% of the effluent sulfur is released as SO_2 and the remainder as SO_3 . SO_3 is a local pollutant; as it leaves the stack, it reacts with water vapor to form an acid mist of dilute H_2SO_4 droplets. This mist may fall near the plant, causing corrosion of metal surfaces. Some of the SO_3 may leave the stack as "acid smut". This material is formed by SO_3 condensation on cool spots inside the stack (below about 280°F) and adsorption onto flakes of carbon, which are deposited simultaneously. Where growth occurs on metal surfaces, corrosion produces ferric sulfate which is incorporated into the carbon flake.

In the following we briefly summarize the properties of the sulfur oxides most significant for flue gas sampling: equilibria, vapor pressures, gas phase oxidation equilibria and kinetics, adsorption properties of SO_2 , and physical chemistry of aqueous solutions of SO_2 . Finally, we discuss conclusions, bearing upon the analysis program, which may be drawn from the data presented.

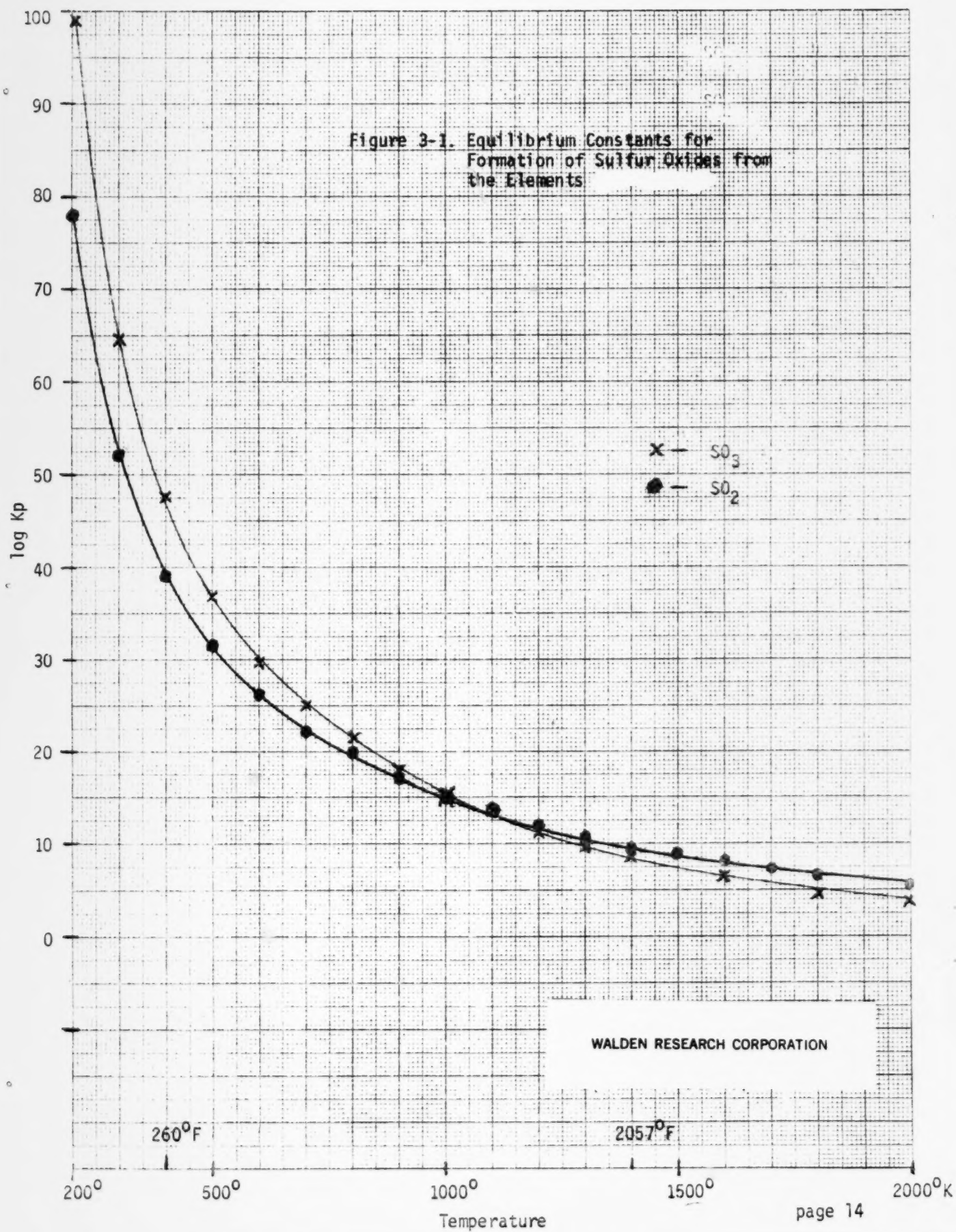
3.2 Properties of SO_2 and SO_3

3.2.1 Equilibrium Constants for Formation of SO_2 and SO_3 From the Elements

The equilibrium constants, K_p , for the formation of SO_2 and SO_3 from sulfur and oxygen are shown as a function of temperature in Figure 3-1 (488) where,

$$K_{p\text{SO}_2} = \frac{P_{\text{SO}_2}}{P_{\text{O}_2} \cdot P_{\text{S}}}, \quad \text{and} \quad K_{p\text{SO}_3} = \frac{P_{\text{SO}_3}}{(P_{\text{O}_2})^{3/2} P_{\text{S}}}$$

Figure 3-1. Equilibrium Constants for Formation of Sulfur Oxides from the Elements



From Figure 3-1, it follows that SO_2 is the stable species at high temperature and SO_3 is the stable species at low temperatures. The composition of the equilibrium mixture as a function of temperature is shown in Figure 3-2.

3.2.2 The Vapor Pressure of SO_3

The vapor pressure of SO_3 between 0° and 100°C is shown in Figure 3-3. Solid (α) SO_3 is the stable form below ca 65°C . The vapor pressures of the less stable solid phases (β, γ) are essentially indistinguishable from that of the liquid.

3.2.3 The $\text{SO}_3\text{-H}_2\text{O-H}_2\text{SO}_4$ Equilibrium

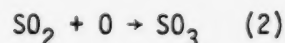
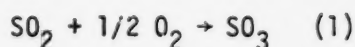
The dewpoint of SO_3 varies with composition in the flue gas, i.e., with the concentrations of SO_3 and H_2O ; the usual dewpoint is about 280°F . Observed dewpoints in a flue gas are discussed subsequently (Section 5). The calculated concentrations of SO_3 and H_2O in equilibrium with pure sulfuric acid are shown in Figure 3-4.

3.3 The Oxidation of Gaseous SO_2

3.3.1 Homogeneous Oxidation

The oxidation of SO_2 to SO_3 has been measured in a furnace (530), where it was found that, at 2-3% O_2 , the ratio of SO_3 to the total SO_x concentration is about 0.04 at 1080°C . This ratio, η' , is an experimental result and not necessarily the equilibrium value. A comparison between η' and the corresponding equilibrium value, η , is given below.

There are two principal mechanisms for the homogeneous oxidation of SO_2 :



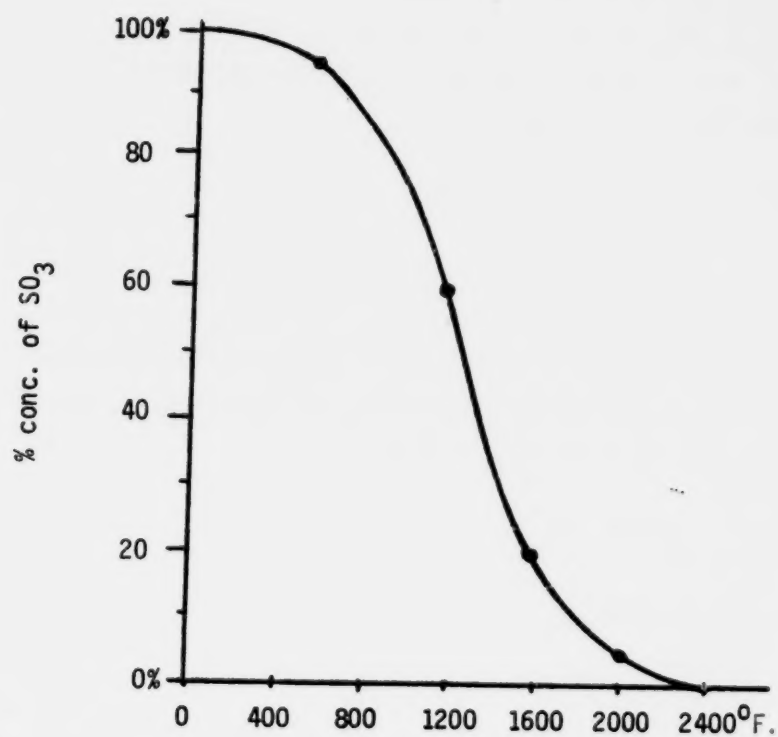


Figure 3-2. Equilibrium Concentration of SO_2 and SO_3 vs Temperature at Atmospheric Pressure (51)

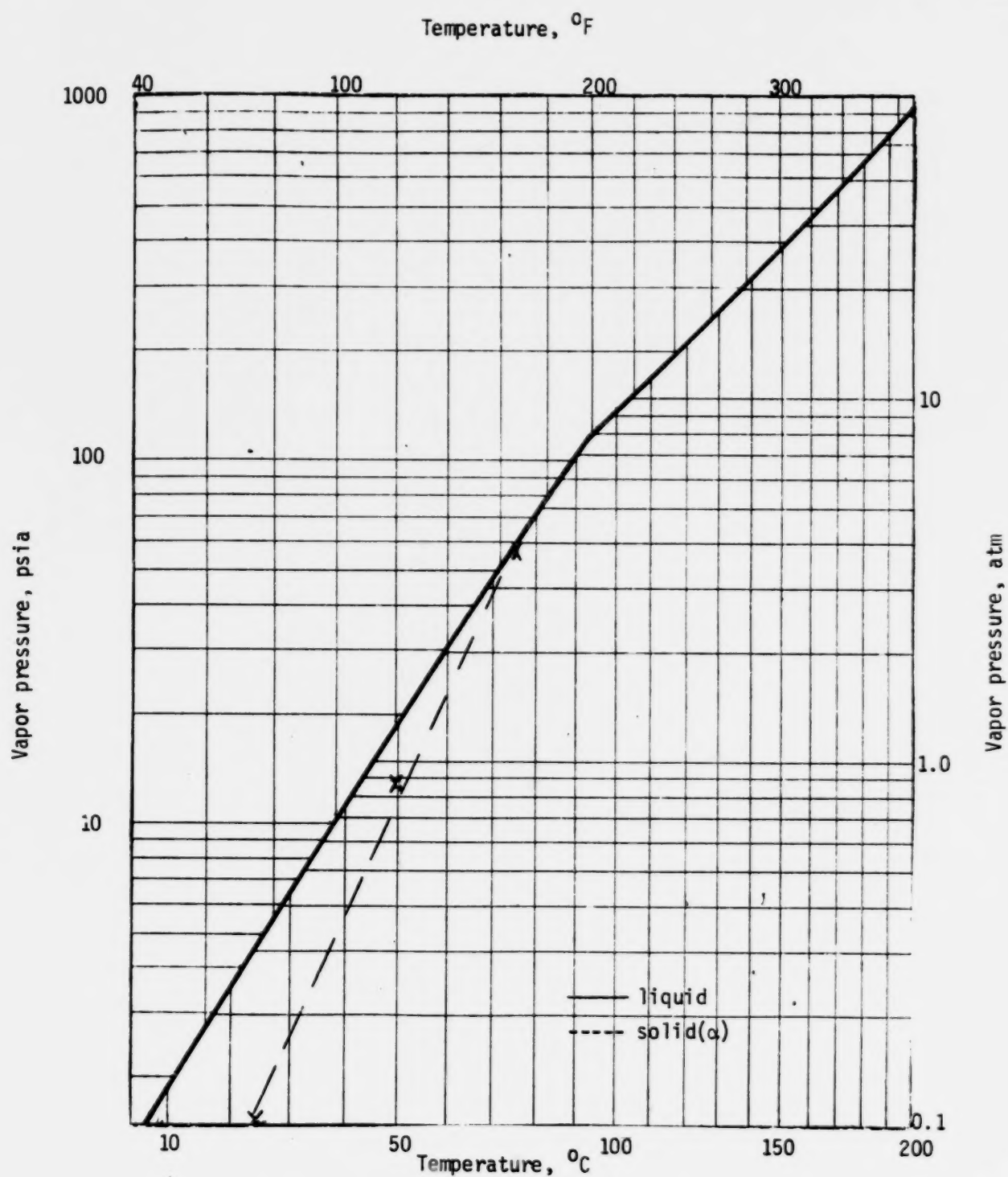
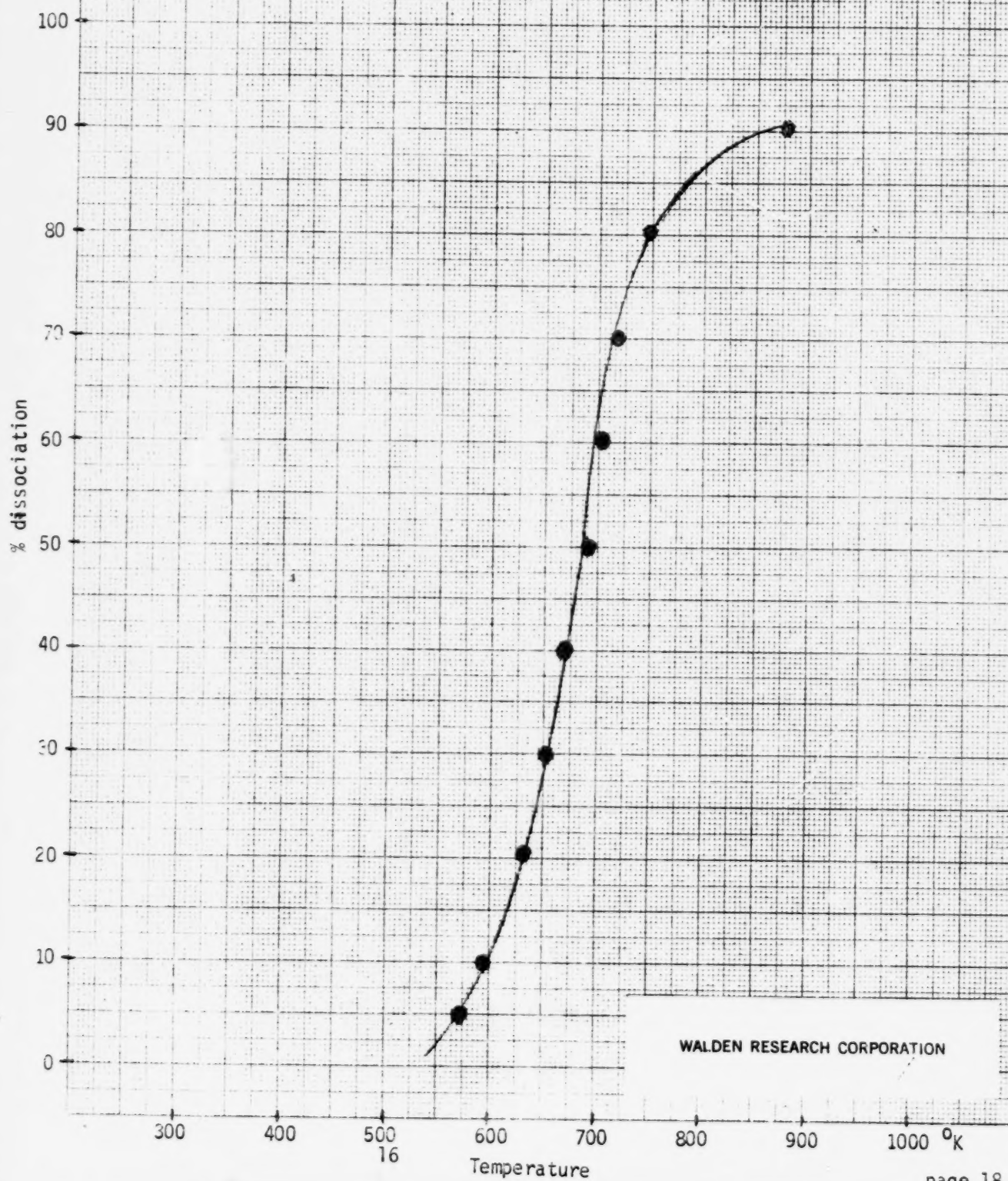


Figure 3-3. The Vapor Pressure of SO_3 (475).

Figure 3-4. The $\text{H}_2\text{SO}_4 = \text{H}_2\text{O} + \text{SO}_3$ Equilibrium

$p = 1 \text{ atm}$



The thermodynamic (equilibrium) data for reaction (1) are shown in Figures 3-5 and 3-6 (530).

The point marked 'x' in Figure 3-6 corresponds to the results previously quoted from reference (51). It is not possible to extend these measurements over a wider range of temperature since the reaction is frozen below about 1000°C under the conditions in a furnace.

It is not known whether reactions (1) or (2) represent the mechanism of SO_3 formation. Evidence from measurements made in H_2S flames that SO_2 is oxidized by O atoms (reaction 2) (485) is: first, there is a close parallel between the O atom concentration and the rate of SO_3 formation and, second, there is no evidence for a molecular equilibrium reaction.

3.3.2 Heterogeneous Oxidation

Many metal oxides catalyze the oxidation of gaseous SO_2 . Vanadium oxide is one of the most efficient and a significant component of many residual oils. Nickel compounds, also present in oil, decompose to nickel oxide, which also catalyze the oxidation of SO_2 . Investigation of this catalytic process is difficult, because the adsorption of SO_2 on the walls changes continuously, particularly where carbon deposition is high (530). However, the rate of oxidation increases with temperature (484).

At 100°-500°C, V_2O_5 is thought to react chemically with SO_2 (51), $\text{V}_2\text{O}_5 \rightarrow \text{V}_2\text{O}_4 + \text{SO}_3$. Ferric oxide oxidizes SO_2 at 800°C by the reaction (474) $3 \text{Fe}_2\text{O}_3 + \text{SO}_2 \rightarrow 2 \text{Fe}_3\text{O}_4 + \text{SO}_3$.

3.3.3 Sulfate Decomposition

Alkali metal sulfates and ferrous sulfate, present in furnace deposits, decompose on heating to product SO_3 . The dissociation temperatures of calcium and magnesium sulfates at one atmosphere, are 1595°C and 1150°C, respectively (476). At 520°C

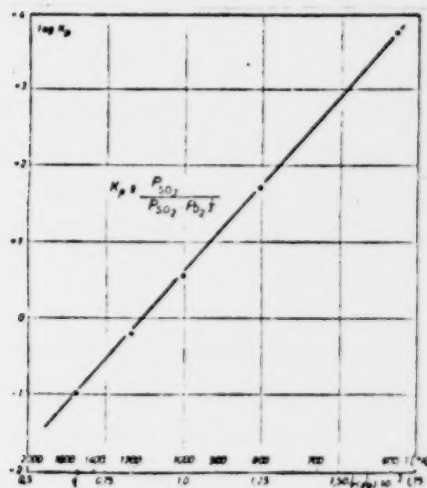


Figure 3-5. The Equilibrium Constant for Reaction (1) vs Temperature

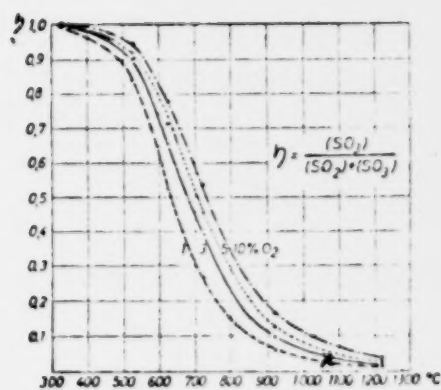


Figure 3-6. The Fraction of the Total SO_2 Which is Oxidized to SO_3 Calculated from the Equilibrium Constant

ferrous sulfate is oxidized to ferric sulfate which decomposes at 650°C.

The decomposition of sulfates has recently been extensively reviewed by Thomas et al (493).

3.4 Adsorption of SO₂

Data on the adsorption of SO₂ on carbon black is given below (Table 3-1). The adsorption isotherms on silica over the range 0-100°C are shown in Figure 3-7. Adsorption on silica gel is almost entirely capillary condensation, rather than direct surface adsorption, as the isotherms fit the Freundlich equation (51), but at 300 and 400°C the adsorption process is complicated by the reaction, $3\text{SO}_2 + 2\text{SO}_3 + \text{S}$.

Many other substances adsorb SO₂; generally much water is adsorbed simultaneously. Salts of the alkali metals, alkaline earth metals and the sulfides of nickel, zinc and iron have also been investigated (491). Many of these substances react with SO₂ rather than adsorb it.

Potentially, carbon is the best sorbent for SO₂, first because its capacity is high and, second, because, in a flue gas, water and oxygen are simultaneously adsorbed and at elevated temperatures oxidize SO₂ to SO₃ and convert the product to dilute sulfuric acid. The collection of (SO₂ + SO₃ + H₂SO₄) would therefore be relatively simple and free from much foreign adsorbed material. Carbon is the closest approximation to a selective (non-reactive) sorbent for total sulfur oxides in flue gases.

3.5 Solution Chemistry of SO₂

3.5.1 The Solubility of SO₂

Solubility data for SO₂ in water and in dilute H₂SO₄ are summarized in Table 3-2. The solubility of SO₂ in water is significant but decreases with increasing concentration of (dilute) H₂SO₄.

TABLE 3-1
 ADSORPTION OF SO₂ ON CARBON BLACK (477)

Temperature °C	6.5	12.0	16.0	18.5	25.5	43.5	56.0	71.0	86.0
Adsorbed Vol. cc/gm Carbon at One Atmosphere	495	408	375	320	261	185	136	97	76
Pressure in mm Hg	827.5	759.5	649.5	551.5	404.5	322.5	258.5	194.5	126.6
Adsorbed Vol. cc/gm Carbon	402.9	379.4	320.8	278.9	235.6	195.4	171.9	140.6	101.5
									60.4
									21.4

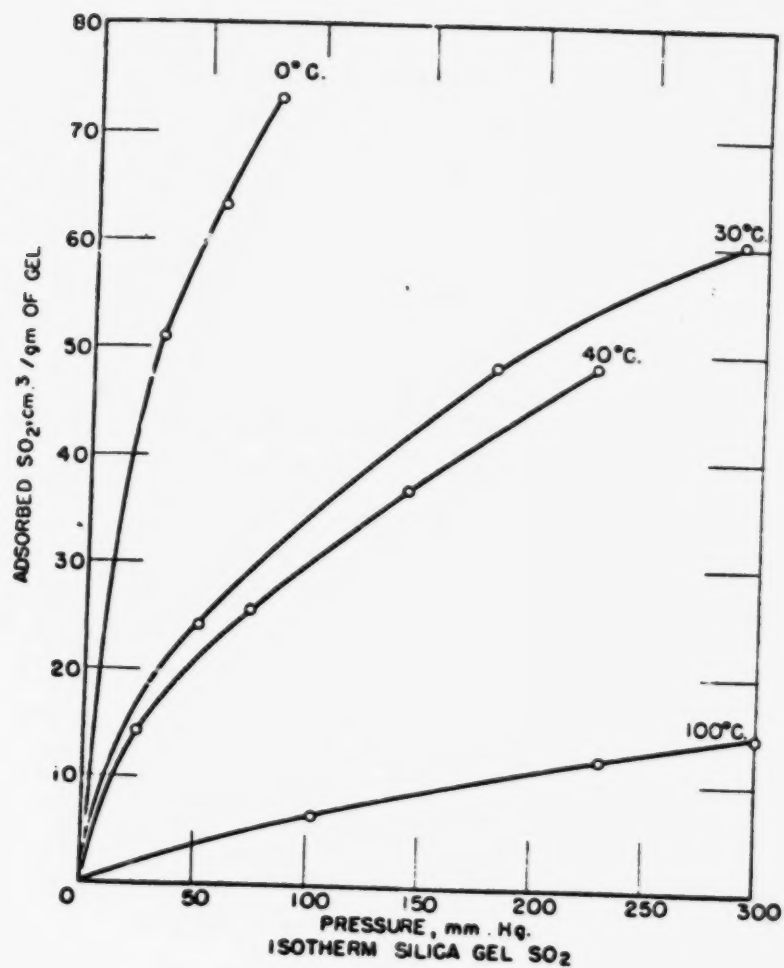


Figure 3-7. Adsorption of SO₂ on Silica Gel (478)

TABLE 3-2
SOLUBILITY OF SO₂

SO ₂ Partial Pressure (atm)	Temp (°C)	Solvent	Solubility g SO ₂ /1000 g Solvent	Reference
1	62	Water	21.5	(482)
1	41	Water	48.1	(482)
1	20	Water	118	(472)
1	0	Water	186	(473)
5.7x10 ⁻⁴	50	Water	0.5	(483)
1.7x10 ⁻⁴	11	Water	0.2	(483)
1	62	10% H ₂ SO ₄	17.1	(482)
		30.3% H ₂ SO ₄	12.6	(482)
1	41	7.3% H ₂ SO ₄	36.5	(482)
		18% H ₂ SO ₄		

In the presence of air and trace concentrations of transition metal ions, the apparent solubility may be greatly increased by oxidation to $\text{SO}_4^{=}$ (549,527). Manganese sulfate (0.0028%) increases the apparent solubility of SO_2 in water by 600% by catalyzing its oxidation to SO_3 . However, the presence of phenol (9) cresol and xlenol as impurities (0.005%) inhibit the oxidation of SO_2 in the presence of Mn^{++} ions; catechol, resorcinol, and pyrogallol and other polyhydric phenols are claimed to stop the reaction completely (but see subsequent discussion of analytical chemistry).

3.5.2 Acid Dissociation Constants

The dissociation constants of sulfuric, sulfurous and, for comparison, carbonic acids are given in Table 3-3 (481).

TABLE 3-3
ACID DISSOCIATION CONSTANTS

	1st	Temp.	2nd	Temp.
H_2SO_4	-	-	2×10^{-2}	18°C
H_2SO_3	1.7×10^{-2}	25°C	5×10^{-6}	25°C
H_2CO_3	3.5×10^{-7}	18°C	4.4×10^{-11}	25°C

The acid strength of H_2SO_3 is comparable to that of HSO_4^- and far greater than that of H_2CO_3 .

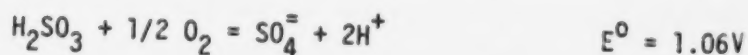
3.5.3 Redox Chemistry

The oxidation-reduction potentials for the sulfite-sulfate couple vs H_2 are (479),

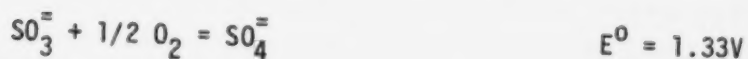
Acid solution	$\text{H}_2\text{SO}_3 \rightleftharpoons \text{SO}_4^{--}$	$E^0 = -0.17 \text{ V}$
Alkaline solution	$\text{SO}_3^{--} \rightleftharpoons \text{SO}_4^{--}$	$E_B^0 = +0.93 \text{ V}$

The standard potentials for reaction with molecular oxygen are (479):

Acid Solution



Alkaline Solution



Junge and Ryan (549) have shown that the aqueous oxidation rate of SO_2 (4 ppm in air) decreased with decreasing pH and ceased at pH 2.2 (in the presence of FeCl_2 catalyst). Berger et al (527) repeated these experiments at 17 ppm SO_2 in the presence of fly ash and found that oxidation ceased at pH $\approx$ 3.

In view of the large favorable potentials, it appears unlikely that thermodynamic factors play a significant role in the acid inhibition phenomenon.

3.6 Conclusions

The general properties of SO_2 and SO_3 , discussed above, have been selected for their bearing on some of the problems and sources of error in flue gas analysis.

The solubility data, for example, show that SO_2 is absorbed in water, but less so in dilute acid. Both SO_2 and SO_3 are obviously soluble in alkali, but the oxidation of SO_2 to SO_3 cannot readily be inhibited in alkali. In water or dilute acid, many organic phenol compounds at least partially inhibit the oxidation of SO_2 to SO_3 , although they are less effective in the presence of ions of the transition metals.

Adsorption data is probably not a useful method for analysis, since even the relatively high absorption on silica gel and carbon is

by capillary condensation and therefore not specific. The oxidative adsorption on carbon may, however, be useful for total sulfur oxides.

The very high adsorption on carbon is an indication of a possible source of error in SO_x analysis where combustion is poorly controlled.

The low vapor pressures of SO_3 and H_2SO_4 , compared to the remaining constituents of the flue gas permits efficient condensation of SO_3 as acid mist.

4. MANUAL SAMPLING METHODS FOR GASEOUS POLLUTANTS

4.1 Introduction

There is no universal method for sampling gaseous pollutants, even where the number of pollutants is quite restricted (as it is here). Changes in the effluent environment due to the variety of source and fuel types, operating characteristics (steady-state vs. transient), and control techniques establish the unreasonableness of developing a single recommended standard method or even a single simplified method for the several contaminants and the wide range of concentrations encountered. Therefore, a number of manual methods for specific situations must be considered. While different in detail, they share common requirements for pre-test planning, sample train components, and determination of velocity, moisture content, temperature and pressure. The brief discussion below outlines these common factors only in the detail necessary to demonstrate the relationship between the various aspects of the program.

4.2 Common Factors

4.2.1 Pre-Test Planning

Analysis of the objectives of an emissions determination, the characteristics of the source and the available resources are essential elements of the pre-test plan. Such factors as steady-state vs. transient operation, lengths of cycles, peak periods of emission, estimated gas composition and pollutant concentrations, gas temperatures, duct size, gas velocity and humidity are examined to select an appropriate collection method, method of analysis, sampling rate, sampling interval, number of tests required for proper statistical analysis, as well as to consider less obvious needs, such as special materials of construction (temperature or corrosion effects, etc.). Such mundane factors as availability of ladders, scaffolding, sampling ports, lighting (for

night work), and coordination with operating personnel must be included in the test plan.

Adequate planning increases the probability for representativeness of the sample which is the real measure of success in the tests to follow. The alternative to pre-test planning is the too familiar trial-and-error method which leads to extended experimental programs, overlooked key data and a generally more costly and less representative result.

4.2.2 Stack Measurements

The initial step in the experimental procedure is to establish the velocity, pressure, temperature, and water content of the stack gases. Velocity measurements are required to permit integration over the cross-sectional area to compute the total volume of effluent. Time dependence of flow rate, temperature and composition should also be observed over a complete operating cycle.

Rigorous methods for velocity measurements (including sampling locations, number of samples per cross-section and their position) are described by Bloomfield (525), ASME (502), Hawksley (537). Industrial and power boilers and heaters are usually designed for velocities of 2000-3000 ft/min, which is a convenient range for pitot tube use. A pitot traverse is generally employed. (See Section 4.3.2.) Small natural draft furnaces found in residential heating produce low velocities (approx. 10 ft/sec) (539). Pitot tubes with conventional manometers or other flow measurement schemes are necessary. (See Section 4.3.3.)

There is much variability in the configurations of the ducts containing the effluent. This may introduce difficulties in establishing the cross section of the duct (necessary for volume and mass flow) and may lead to flow irregularities following bends or constrictions. One is generally advised to sample several diameters downstream and a few diameters upstream of any flow disturbing element. In

practice it is rare to find an ideal location. The deviation from spatial uniformity of flow in a duct is well illustrated in Figure 4-1 (537) which shows the velocity ranges encountered under some test conditions. The necessity of a velocity traverse is obvious. (A review of methods for determination of gas velocity in ducts is presented in Section 4.2.6.)

The pitot sampling points are frequently used subsequently as contaminant sampling points. Stack temperature, pressure, and moisture content must also be measured to compute contamination at stack and standard conditions. Temperature and moisture content generally change in the sampling system and the volumes indicated by the sample flow meter must be corrected back to the initial conditions. The BSI (379) method is satisfactory for determination of the moisture content of the flue gas.

4.2.3 Sampling Train Components

4.2.3.1 General

The apparatus used for the manual sampling of gases has been divided into modular components. A typical array of sampling system components is shown in Figure 4-2 [after Bloomfield (525)], which depicts, schematically, a duct, sampling nozzle, probe (sometimes temperature-controlled), collection device, water condenser and/or dessicant column, sample flow meter, (gas temperature, pressure and water content at the meter are essential), and air mover. Analogous sampling arrays are discussed by American Congress of Government Industrial Hygienists (540), Arthur D. Little, Inc. (541), ASME (502), Hawksley (537), "Air Pollution Source Testing Manual" (1), ASTM (547), Manufacturing Chemists Association (542), and Industrial Gas Cleaning Institute (543).

For gas sampling the nozzle design is not critical, although provision is frequently made for a simple preliminary

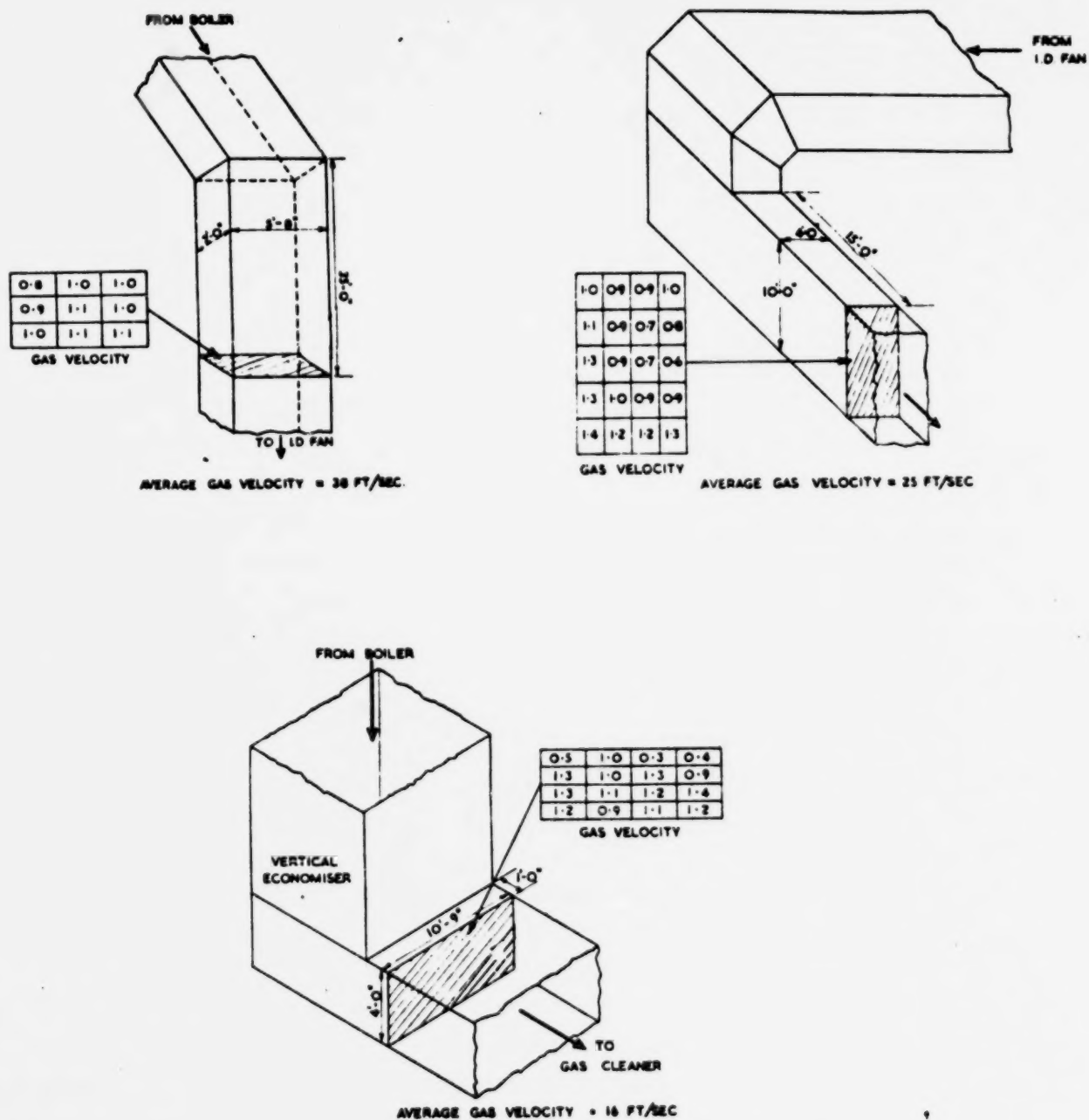


Figure 4-1. Observed Variations of Flow in Ducts
(After Hawksley) (537)

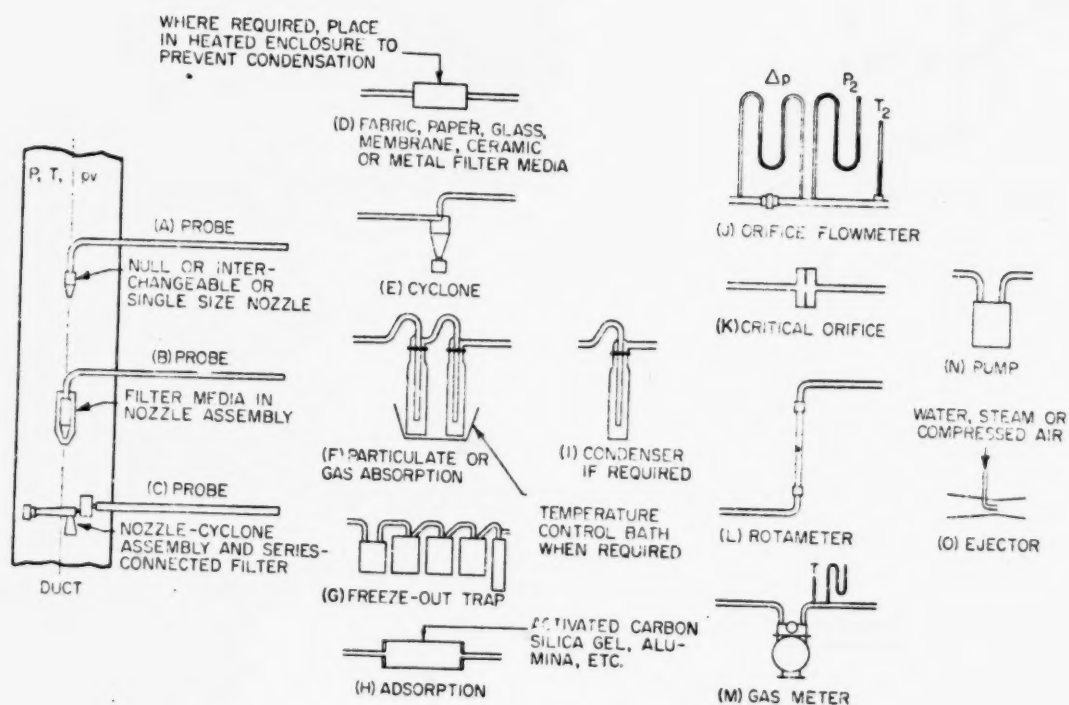


Figure 4-2. Sampling System Components
(After Bloomfield) (525)

filter to remove combustion particulates which may interfere with the analysis or be destructive to meters, pumps, etc.

Probes are of two general classes, simple and temperature-controlled. Probes are frequently heated to prevent loss of sample through condensation. The effectiveness of this technique in sampling for SO_2 and SO_3 is shown by Lisle and Sensenbaugh (80). Alternatively, one can use a simple probe, but one must use very careful handling techniques and quantitatively wash condensate and precipitate from the probe and sampling lines. This material is then combined with the material in the collector. This approach increases the opportunity of error and is generally undesirable. Cooled probes are used where one is sampling directly in the furnace at temperatures above about 800°F.

Gas sample collecting devices may be divided into two classes, those which concentrate a sample and those which do not. The latter are sometimes called grab samplers and simply retain a gas sample for subsequent analysis in the laboratory. Most of the familiar methods, i.e., absorption, adsorption, condensation, or freeze-out are concentrating mechanisms. Of these, by far the most used is absorption.

In liquid absorption effectiveness is determined by:

- contact between gas and absorbent
- rates of diffusion and mixing
- solubility in or reactivity of the absorbent
- volatility of contaminant
- concentration of reactant in absorbing solution
- volumes of gas sampled and absorbent

Clearly, the selection of a specific contaminant collection system must be carefully made. Scrubbing efficiency (discussed below) cannot be assumed to be complete and quantitative.

A variety of adsorbents are available for gas sampling, although the most used is active carbon. The adsorbed gas is then removed by heat or eluted by a carrier gas. Solvent stripping and vacuum removal may also be used. Other adsorbents in common use are silica gel, lithium chloride, alumina and fuller's earth.

Condensation or freezeout methods are also employed. Condensation is commonly used to remove water from the combustion gases prior to metering and may be used for specific contaminants such as SO_3 . The temperatures required to collect a given contaminant depend upon its properties.

Grab samples are taken in bottles or flasks and several types of plastic bags or balloons. Plastic bags have the advantage that there is no pressure change on filling or withdrawal of the sample.

Some precautions which also apply to other collecting devices, are most important in grab sampling, since samples are sometimes retained for an appreciable time prior to analysis. Specifically, these problems include chemical interactions in the sample, photochemical decomposition, adsorption on container walls, and leaks.

Indicator tubes are a special class of commercially available grab samplers for specific gaseous contaminants. A granular solid treated to produce a color reaction when exposed to a specific contaminant is confined in a glass or plastic tube. A "known volume" sample is then drawn through the tube (usually with a squeeze bulb or piston pump) and the concentration of contaminant is determined by the existence and length of the color stain in the tube. Treated papers and paints based upon the same principle have also been used.

Sample metering is required for a complete system. For a specific sampling system, one must select from the following types of meters: constriction types (orifice, nozzle, venturi), dry gas, wet test, rotameters, positive displacement (rotary, piston, gasometer), turbine, laminar flow (capillary), deflection vane, vane anemometer, and evacuated tanks (pressure differences compensated for temperature). For a complete mechanical description, see Jacobs (507), Altieri (533) or the AGA Manual (534).

A manual sampling method demands ruggedness and portability and must be able to tolerate corrosive combustion products. Based on these considerations and accuracy requirements, a number of metering techniques may quickly be eliminated. Final selection will thus be made from the following, more restricted group: dry gas, orifice, nozzle or venturi, capillary, rotameter, and evacuated tanks. All of these devices must be carefully calibrated at their operating conditions. Pressure, temperature, and water content at the meter must be known in order to correct the combustion gas sample back to initial conditions.

Air movers must be able to overcome the pressure drops in the sampling system at the required gas flow rate. The following types of air movers have been used: turbine blower (high volume, low pressure differential), mechanical vane pump (high pressure differential, moderate volume), mechanical piston, diaphragm, or positive-displacement gear pump (high pressure differential, high volume), air, water, or steam ejectors (low pressure differential, moderate volume, useful in hazardous atmospheres, and where electricity is unavailable), pressure difference in the system (special cases only), and evacuated tanks.

Flow control can be achieved in several alternative ways, viz: a valve between the flow meter and the air mover, a bleed or recycle valve at the air mover inlet, speed control of the air mover motor (usually varying the input voltage to a universal motor), or a constant flow constriction (can be used as flow

meter also; requires vacuum source able to maintain sonic flow through orifice and cannot be used for an on-off control). Further analysis is presented in Section 4.2.3.2, following.

Materials of Construction - The materials of construction are often a major factor in selection of components. Corrosive species of the environment may react with container walls and destroy the sample as well as the equipment. For example, ASTM (D1605) cautions against the use of metal containers for H_2S , SO_2 or oxides of nitrogen. Most sampling devices are made of glass or plastic although specific stainless steels can be used. Concern about proper selection of materials of construction is reduced downstream of the collector, although it is still necessary to insure reasonable equipment life.

4.2.3.2 Evaluation of Specific Components

Sample Metering Device - The accuracy of an emission determination depends as much upon the accuracy of sample gas volume measurements as upon the analysis. This implies that suitable sample gas metering devices must provide measurement with errors of 1% or less. Within this accuracy constraint, the particular measuring device will be selected in harmony with the pollutant collection scheme and within the general engineering design requirements of:

- a. portability
- b. instrumental and operational simplicity
- c. reliability and
- d. ruggedness

For manual sampling systems for SO_x pollutants in flue gas streams, the critical orifice is the best engineering solution for sample gas measurement. When calibrated, critical orifices meet the measurement accuracy requirements plus the design requirements listed above. The collectors used in an SO_x system are a condenser for SO_3 and midget impingers for SO_2 . In order to obtain high collection

efficiency, this system will operate at flow rates of three liters per minute or less. It is not necessary to vary the flow rate during sampling; hence, discrete flow rate selection is satisfactory. Critical orifices are commercially available (Millipore Corporation, Bedford, Mass.) in flow rates that include 0.5, 1.0 and 3.0 l/min. These devices are made of stainless steel, weigh 3 grams, and occupy a volume of less than a cubic centimeter. It is obvious that these devices are readily portable and instrumentally simple. They are mechanically rugged; hence, no special handling techniques are required to prevent damage during field use. Since the flow rate is set by the particular orifice, operation simply requires starting the sampling pump and measurement of the sampling time. Sample gas pressure and temperature must of course be measured for density corrections, and the pressure differential across the orifice noted to assure that critical flow conditions through the orifice are maintained.

Other sample gas measuring devices which may be satisfactorily used in SO_x source sampling are summarized in Table 4-1. However, they are obviously not the simplest instrumental or operational solutions.

Air Movers - For the SO_x system the selection of air movers is limited to mechanical pumps which can maintain the critical pressure drop across a 3 l/min critical orifice when connected to the sampling system. A particularly convenient pump is an eight pound, oil-less, motor-vacuum pump unit (Gast Model 1531). Based on our experience, this unit is readily portable, reliable and rugged. Similar units should also be satisfactory.

TABLE 4-1
COMPARISON OF SATISFACTORY GAS METERS FOR SO_x SAMPLING

Meter	Typical Best Accuracy	TOTAL VOLUME GAS METERS					Remarks
		Portability	Instrumental Simplicity	Operational Simplicity	Reliability	Field Ruggedness	
Wet Test Meter	±0.5%	Very Poor	Fair	Good	Good	Poor	Mainly a lab instrument
Dry Gas	~±1%	Good	Fair	Good	Fair (frequent cal. neces- sary)	Good	Poor for flow <3 l/min
Rotary Gas Meter	~±1% (large vol.)	Poor	Fair	Good	Good	Good	Not commonly available for small flows
Constant Vol. Evac. Tank	~±1%	Good	Good	Fair	Good	Good	Total sample volume must be smaller than tank volume

TABLE 4-1 (Cont.)

Meter	Typical Best Accuracy	GAS FLOW METERS					Remarks
		Portability	Instrumental Simplicity	Operational Simplicity	Reliability	Field Ruggedness	
Calibra- ted Ori- fice Meter	±1 to 2% (with care- ful cali- bration)	Good	Good	Fair	Good	Good	Sample volume calculated as a function of flow and time
Capil- lary Flow Meter	±1 to 2% (with care- ful cali- bration)	Good	Good	Fair	Good	Good	(Same as Above)
Venturi Meter	±1 to 2% (with care- ful cali- bration)	Good	Good	Fair	Good	Good	(Same as Above)
Rota- meter	±1 to 2% (cali- brated with flue gas)	Good	Good	Fair	Good	Fair	(Same as Above)
Mass Flow Meters	~±2%	Fair	Poor	Good	Information not avail- able	Fair	Recorder output available

4.2.4 Representative Stack Sampling for Gases

The classical problem of stack sampling for gases is to associate the (average) samples* taken generally at different times and positions, with either an average concentration, or with greater difficulty, an average throughput. The precision and accuracy of the determination are a function of the method(s), the experimental design and the variability of the source. In any sampling program, one must specify the desired precision as determined by the purpose of the work, before the magnitude (or even the feasibility) of the sampling program can be established.

Before attempting high precision analysis of total emissions, it is necessary to identify and distinguish variability in the source from error and imprecision introduced by the methodology. "True" variability will exist in total flow and in component concentrations, as functions of time and location in the duct. Each measurement (velocity, duct size, sample flow rate, sampling time, mass of contaminant, etc.) will have an associated error. As a result of the finite number of replications there will be an associated imprecision to the limiting means and, finally, since only a finite number of locations are selected, there will be an associated imprecision in mapping the flow field.

Flue gas flow measurement techniques are reviewed in Section 4.2.6, following, which discusses velocity measurements, duct traverses, calculation of volumetric flow and their associated errors. Sampling locations in ducts and sampling errors are discussed in Section 4.2.7.

*The collection of a gas sample which accurately represents the flow at a given point is far simpler than the complexities of representative particulate sampling. Isokinetic sampling rates are not a requirement since the (thermal and turbulent) eddy diffusivities are far too large to permit significant molecular fractionation in the very weak centrifugal fields imposed by any velocity mismatch attainable in sampling (523).

Errors in manual sampling methods are discussed in Section 5; the observed precision and accuracy of field determination of sulfur oxide concentrations are discussed in Section 6.

"True" variability in contaminant concentration in both location and time is best approached by rapid response instrumental methods. Gross variations in contaminant concentration caused by poor mixing of infiltration air can be indirectly compensated by profiling (and monitoring) with a continuous oxygen or carbon dioxide analyzer and suitable selection or weighting of sampling points. (See Section 4.2.5, following.)

In large coal-fired power plants, short term fluctuations are far greater than longer term variations. Slag buildup from boiler tubes (soot-blowing) may be removed every few hours; thus, the week to week variations in average gas temperature due to slag buildup is less than the hour to hour fluctuations. Coal supplies, delivered to large plants from a number of mines and different seams also contribute to source variation.

A summary of the short and long term variances in ash and sulfur content of coal samples taken from the feed to a large power plant is given below (494):

	<u>% Ash</u>	<u>% Sulfur</u>
Long-term variance (weekly)	0.31	0.12
Short-term variance (hourly)	0.72	1.05

Thus the hour-to-hour fluctuation in ash and sulfur content (and the SO_x content of the flue gas) is undoubtedly greater than the week-to-week fluctuations.

It is thus clear that no single, a priori, experimental plan can be drawn up which will optimize a given emissions

output determination. The plan will be a function of the resources allocated, the accuracy desired, and the nature of the source.

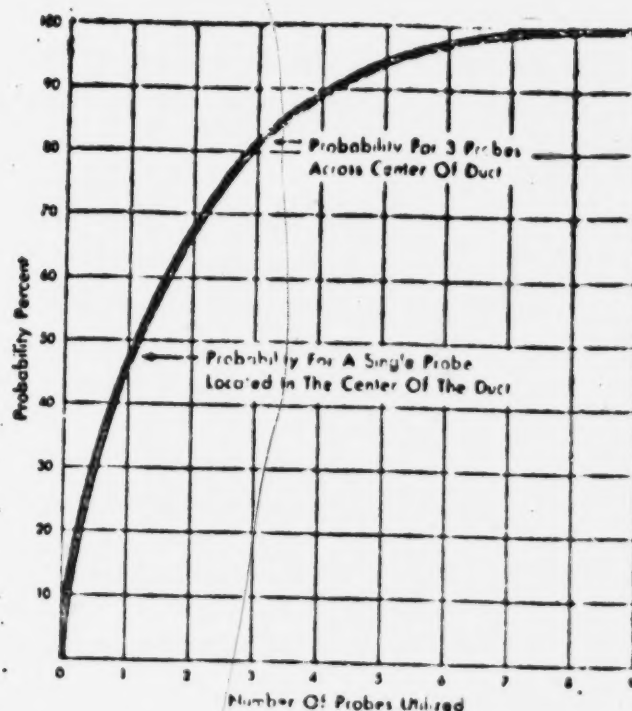
4.2.5 Sampling Errors in Ducts

Literature on sampling locations for obtaining representative average concentrations of gases within ducts is scarce. Although this subject is frequently discussed in the literature for particulate sampling, the discussions are concerned with inertial separation of particles from the gas stream. Since inertial separation of pollutant gases from carrier gases does not occur, the particulate sampling discussions are not generally applicable (i.e., isokinetic sampling is not necessary and stratification due to duct bends, etc. is not present).

There is a widely held belief that gas stratification is not present in ducts with turbulent gas flow (613). However, eddy diffusion studies (571) show that a straight duct length of the order of 10^2 duct diameters is required for good mixing of a highly stratified gas. It follows that in many large scale combustion systems where infiltration air is known to occur there is no direct location where the gas is well mixed. Luxl (524) carried out a total of 792 Orsat oxygen traverses in 10 different ducts of fossil fuel combination sources. He found (Figure 4-3) that stratification is generally present and that single point samples are usually non-representative in large ducts.

ASME (502) specifies a multi-point sampling system for Orsat analysis of flue gases and a single point sampling system for SO_3 and SO_2 , but there is no discussion of this inconsistency. The multi-point locations specified without discussion are then also selected by ASME for velocity traverse. It may be argued that velocity traverse schemes can give representative average velocities in a duct where the velocity profile is not generally flat; hence,

Figure 4-3. Probability of obtaining an accuracy within 15% of 9 point analysis for O_2 in a large duct (524).



the same techniques should give representative values of emissions. However, until a careful study is made the accuracy of this technique cannot be defined. (Compare Section 4.2.6, following.)

The emission of material from a combustion source is described by the general equation,

$$E_a = \int_A C_a \vec{v} \cdot \vec{n} dA ,$$

where E_a is the emission of material (a), C_a is the concentration of (a), $\vec{v}$ the flue gas velocity along the duct, A is the cross sectional area of the duct, and $\vec{n}$ the unit vector normal to A . It follows from Equation (1) that C_a and $\vec{v}$ are coupled if neither is constant across the duct; hence, they should be measured together.

A traverse using a continuous oxygen or carbon dioxide analyzer can quickly determine the extent of infiltration air stratification. If the gases are not significantly stratified, the pollutant gases may be assumed to be well mixed and the concentration

determined from a single sampling point. However, it is more prudent to sample at more than one point as a check on the mixing of the pollutant gases.

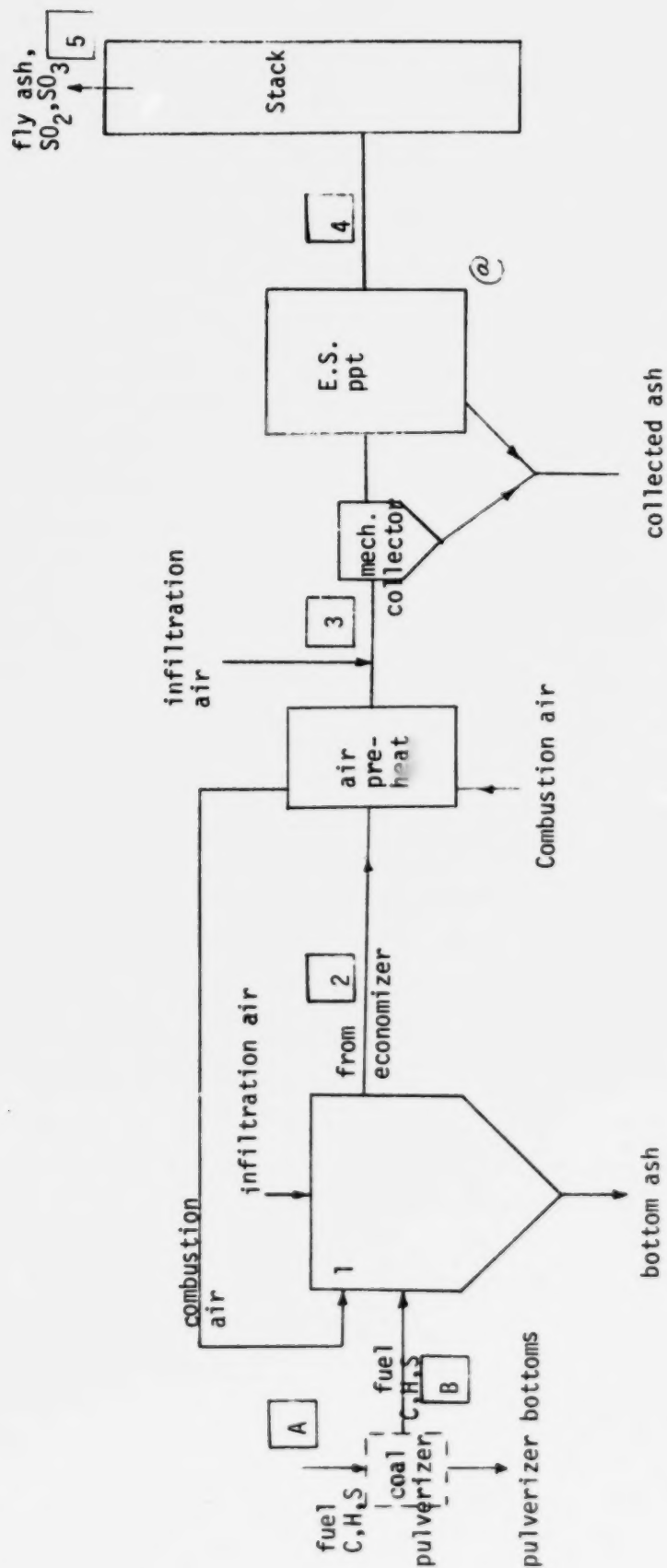
For rigorous measurements a set of replicate samples should be taken at traverse points and a statistical analysis performed in order to establish the flow pattern and estimate of the residual error. For subsequent measurements in this duct, fewer sampling points can be used and the accuracy predicted (537).

Methods for the determination of C_a and V for irregular distributions are discussed in Sections 4.2.6 and 4.3, following.

4.2.6 Variance of Concentration in Large Ducts

A major problem in the high precision determination of pollutant emissions is the variation of species concentration which may exist in a large duct as a result of air infiltration and poor mixing (stratification). In the course of NAPCA's extensive studies of coal-fired power plant effluents (548) many CO_2 concentration profiles were obtained by traverse of large ducts at different sampling locations. The following discussion, based upon a random selection of this test data and, therefore, incomplete, outlines the magnitude of the problem and the influence of both sampling location and equipment type on the results obtained.

Typical sampling locations are illustrated in the power plant schematic (Figure 4-4). The most common locations are at the entrance and exit of the dust collection equipment. The statistical treatment adopted was to calculate the mean CO_2 concentration for each traverse plane, the standard deviation from the mean, and the coefficient of variation ($CV = 100 \sigma/\text{mean}$). Two examples, illustrating relatively homogeneous and stratified flows are given in Figure 4-5. The observed coefficient of variation of



occasionally the E.S. precipitator may be upstream of the air-preheater

(a)

A Plant input data

1

Flue gas sampling points

1

Figure 4-4. Schematic Large Combustion Unit

"HOMOGENEOUS"

1.03	1.00	0.98	1.00	1.01
1.03	1.01	0.98	1.00	1.01
1.00	1.01	0.98	1.01	1.01

3'3"

22'

Ave CO₂ = 11.7%

CV = 1.5%

"STRATIFIED"

.74	.92	1.0	1.0	.97	.95
.82	1.01	1.02	1.01	1.00	.90
.75	1.05	.99	1.02	1.01	.90
.82	1.00	.93	.93	1.01	.86

4'8"

14'10"

Ave CO₂ = 12.6

CV = 9.3%

Random selection from six plants.

Figure 4-5. Normalized CO₂ Traverse Data at Dust Collector of Coal-Fired Power Plants.

the CO₂ concentration is given in Table 4-2 as a function of sampling location. The relatively low value of CV at the outlet of the dust collector, presumably the result of good mixing, suggests this to be the location of choice for both simplicity and good precision. The relatively high value of CV at the inlet to the dust collector may be associated with air infiltration at the air preheater, a common occurrence.

The most frequent sampling locations for emissions determinations are the inlet and outlet of the dust collectors. The coefficient of variation of the CO₂ concentration at these locations is given in Table 4-3 as a function of equipment type. With the exception of Plant No. 3, CV at the inlet is relatively large compared to the outlet values.

Conclusions which may be drawn from these data are:

1. CO₂ (or O₂) traverses are extremely valuable for selection of sampling locations and determination of the number of samples required for a high precision emissions determination. CO₂ traverse data may be utilized for normalization of SO_x concentrations made at the selected locations.

4.3 Flue Gas Flow Measurement Methods

4.3.1 Introduction

The emission of a material from a combustion source is described by the general relationship

$$E_a = \int_A C_a \vec{v} \cdot \vec{n} dA \quad (1)$$

where E_a is the emission of material (a), C_a is the concentration of (a), A is the cross sectional area of the flue or duct in question, $\vec{v}$ is the velocity and $\vec{n}$ is the unit vector normal to A .

TABLE 4-2
OBSERVED COEFFICIENT OF VARIATION FOR CO₂ TRAVERSE
AT VARIOUS SAMPLING LOCATIONS

Sampling Position	T ⁰ (F)	No. of Traverse Points	CO ₂ (CV), %
Furnace (1)*	2400	12	4.0
		12	5.2 >4.6
Economizer Inlet (2)	860	8	3.8
		8	3.8 >3.8
Economizer Outlet (3) (Dust Collector Inlet)	360	24	7.1
		24	5.4 >6.2
Outlet of Dust Collec- tor (4)	350	18	3.2
		18	3.2 >3.2

- (2) Sampling should be conducted at the outlet of dust collectors in the absence of other information.
- (3) For simplified methods, single point sampling at the dust collector outlet appear to be feasible (CV < 5%).

* See Figure 4-4.

TABLE 4-3
OBSERVED COEFFICIENT OF VARIATION FOR CO₂ TRAVERSE FOR VARIOUS COAL-FIRED PLANTS

Plant No.	Type of Boiler Firing	Dust Collection Equipment	Sampling Location	No. of Traverse Points	CO ₂ (CV), %
1	Horizontally Opposed	C	I 0	24 12	9.3 2.3,1.4
2	Cyclone	E	I 0	24 24	4.6 3.2
3	Spreader Stoker	C	I 0	18 9	1.5 1.02
4	Corner	C,E	I 0	18 12	8.8 0.97
5	Vertical	C,E	I 0	24 12	7.1 3.2

C = cyclone
E = electrostatic precipitator
I = dust collector inlet
0 = dust collector outlet

If the concentration is not a function of position, i.e., no stratification exists, then Equation (1) can be written as:

$$E_a = C_a \cdot V \quad (2)$$

where

$$V = \int_A \vec{v} \cdot \vec{n} dA \quad (3)$$

which is the volumetric flow.

This discussion is limited to determining the volumetric flow of flue gases from fossil fuel combustion sources.

The technology of measuring subsonic gas flow is not rapidly changing at this time, and the existing techniques have been well documented, including the magnitude of expected errors for laboratory conditions using clean, dry gas. Where field conditions allow the rigorous implementation of some standard test procedure, e.g., ASTM, ASME, ASHRAE, BSI, etc., the flow measurement should be accurate to well within 5%, with the accuracy dependent upon the particular measuring instrument used.

In many cases, flue gas flow measurements will have to be made in gas streams where the flow may be asymmetric, varying in time, particle laden, or of low velocity. The accuracy of measurements made under these conditions cannot be estimated with confidence. In fact, the accuracy will depend significantly on the skill and care of the investigator.

4.3.2 Pitot Tube Traverse

The pitot-static tube traverse is the most commonly used method of measuring gas flows in flues and ducts. In this technique, a pitot-static tube (see Figure 4-6) is inserted through a breaching in the duct wall and a number of velocity measurements are

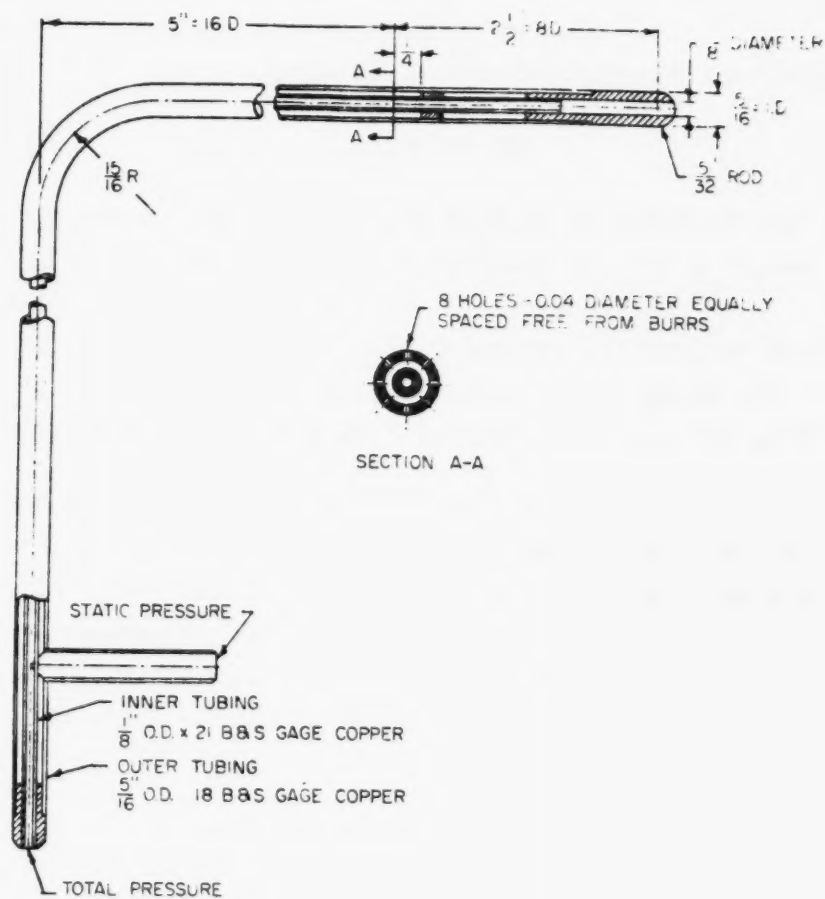


Figure 4-6. A standard pitot-static tube (525).

made across the duct in a plane perpendicular to the flow direction. From the velocity measurements and locations, the integral in Equation (3) is evaluated by numerical or graphical techniques to give the volumetric flow.

4.3.2.1 Velocity Measurements

Interpretation of velocity measurements using a pitot-static tube depends upon the relationship

$$\Delta P = K \frac{1}{2} \rho v^2 \quad (4)$$

where ΔP is the differential pressure between the static ports and the pitot tube; v is the gas velocity; ρ is the mass density of the gas, and K is a calibration factor of the pitot-static tube. Values of K have been measured for various types of pitot-static tubes and for most engineering work (gas speed errors within 1%) K can be taken as unity. Some observed values of K are presented in Table 4-4.

Equation (4) and the values of K given above apply only to pitot-static tubes with a zero angle of attack. The effects of non-zero angles of attack are shown in Figure 4-7. Where the direction of flow is not known within 20° to 30° , or where turbulence exists which changes the angle of attack within these limits, the hemispherical nosed probe will still measure gas velocity to within 2.5% ($v \propto p^{1/2}$).

A practical limitation of the pitot-static tube for measuring flue gas velocity exists for low velocities due to the limiting sensitivity of the manometers which can be conveniently used in field work. For a calibrated inclined manometer, the limiting threshold is about 15 feet per second for an error within 1% (606). Measurements of lower velocities will result in larger errors.

A Staubscheibe pitot tube (Figure 4-8) which has a K greater than unity is sometimes used to measure low velocities.

TABLE 4-4
PITOT-STATIC FACTORS AT LOW AIR SPEEDS (606)

Air Speed (Air at 15°C and 760 mm Hg) (ft/sec)	Tapered-Nose Tube		Hemispherical-Nose Tube	
	Reynolds No.*	K	Reynolds No.*	K
2	330	1-020	335	1-055
4	655	0-989	670	1-006
6	985	0-995	1000	1-001
8	1310	0-992	1335	0-996
10	1640	0-991	1670	0-992
12	1970	0-992	2005	0-991
14	2295	0-995	2340	0-992
16	2625	0-998	2675	0-996
18	2950	0-999	3005	0-999
20	3280	1-000	3340	1-001

*The Reynolds numbers for the two instruments at the same air speed differ slightly because the outside diameters were not the same; they were 0-307 in for the tapered nose and 0-312 for the hemispherical nose.

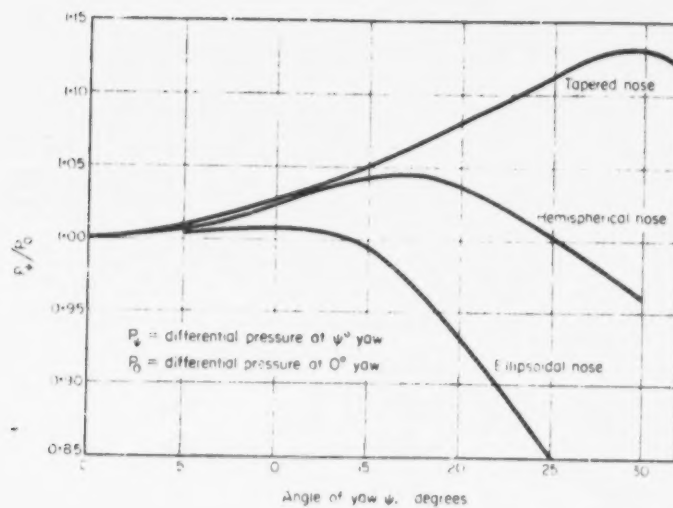


Figure 4-7. Effect of yaw on pitot-static combinations (606)

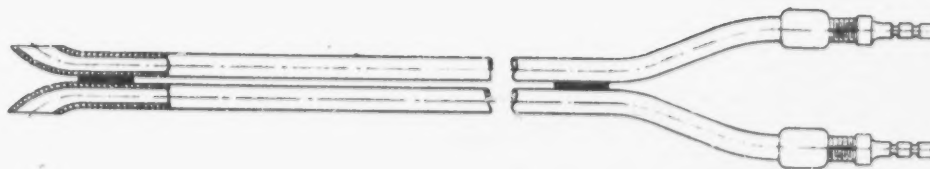


Figure 4-8. Staubscheibe Pitot Tube

However, K varies appreciably with velocity for this device as shown in Figure 4-9, and each tube must be calibrated over the velocity range of the intended measurement.

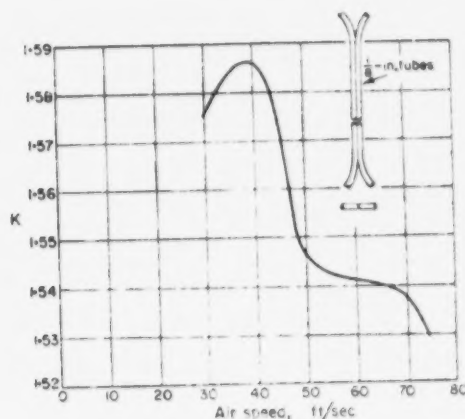


Figure 4-9. Calibration Factors, K , for Staubscheibe Pitot Tube (606)

Since K varies rapidly with velocity, it is likely that intrinsic errors will exist for measurement of turbulent flows.

The Staubscheibe tube is frequently recommended for velocity measurements in particulate laden gas streams because it does not have small static ports which may be plugged (607,525). However, purging systems can be constructed for the pitot-static tubes which force compressed air through the static ports before making a velocity measurement (608). In locations with particulate-laden gases where compressed air is readily available, the purged pitot-static tube is preferable to the Staubscheibe pitot-tube.

4.3.2.2 Traverse

Measuring gas stream velocities at various points across a flue or duct is a velocity traverse. From the geometry of the ducts and the geometry of the traverse point, the gas velocities may be used to calculate the volumetric flow. This

calculation is the evaluation of the integral in Equation (3). The integral may be evaluated graphically; however, the most common technique is to divide the test section into a number of equal area zones and determine the mean velocity in each zone. The velocities for each zone are averaged and the volumetric flow is given by

$$V = \bar{v}A \quad (5)$$

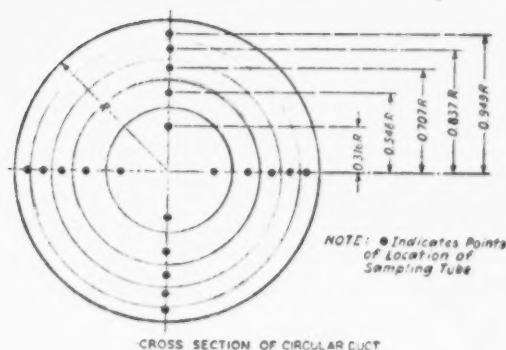
where $\bar{v}$ is the average velocity and A is the area of the test section.

Discussion of techniques for dividing test sections into equal area zones will be limited to ducts of circular and rectangular cross section, since sampling in ducts of other forms is rare. For ducts of unusual shape, the volumetric flow should be determined by graphical integration for accurate results.

The number of test zones that a flue is divided into will depend upon the uniformity of velocity distribution and the accuracy desired, not upon the size of the duct, since for any two similar ducts (different only in size) with similar velocity distributions, an equal number of velocity readings will be required to determine the average velocities with equal accuracies. However, in practice, the size of the pitot tube will limit the number of velocity measurements in small ducts.

4.3.2.2.1 Equal Area Division of Ducts of Circular Cross Section

The tangential method divides a duct of circular cross section into n equal zones, a circular central zone and $(n-1)$ annular zones (Figure 4-10). Each zone is divided into two equal area annular parts and the velocity measurement is made at the radius of the boundary between the equal area parts. The mathematical derivation of the division of a circular cross section by this technique is found in Ower (606). The method of dividing a circular duct by this technique is shown in Figure 4-10.



Formula for determining location of points in circular duct

$$r_p = \sqrt{\frac{2R^2(2p-1)}{n}}$$

where r_p = distance from center of duct to point p
 R = radius of duct
 p = sampling point number. To be numbered from center of duct outward. All four points on same circumference have same number.
 n = total number of points

NOTE: r_p will be in same units as R .

Example: Duct radius = R ; 20 points total.
 Distance to point 3 = r_3 .

$$r_3 = \sqrt{\frac{2R^2(2 \cdot 3 - 1)}{20}} = \sqrt{\frac{2R^2 \cdot 5}{20}} = \sqrt{\frac{5R^2}{20}} = \sqrt{\frac{R^2}{4}} = \frac{R}{2} = 0.5R$$

Figure 4-10. Tangential Method for Duct Division (609)

The log-linear method is an alternative which gives higher accuracy. The circular cross section is again divided into equal area annular zones, but the velocity is not arbitrarily measured at center of area of each zone. Instead, the measurement points are calculated on the basis of an empirical analysis of the flow through circular pipes. The development of this method, including the determination of the measurement points may be found in Ower (606). The results are summarized in Table 4-5.

For fully developed flow, Winternitz (606) found that a four point log-linear traverse gave an error of less than 0.5%; whereas, the 10 point tangential method overestimated the mean velocity by about 1%. For non-fully developed flow, the 10 point tangential technique was somewhat better than the four point log-linear, but, an eight point log-linear method was superior to the 10 point tangential method. The 6 point log-linear method will give results with an error less than 1% in flow distributions as asymmetric as shown in curve A of Figure 4-11 (606).

TABLE 4-5
LOCATION OF MEASURING POINTS FOR LOG-LINEAR METHOD (606)

No. of Measuring Points Per Diameter	Distance from Wall in Pipe Diameters
4	0.043, 0.290, 0.710, 0.957
6	0.032, 0.135, 0.321, 0.679, 0.865, 0.968
8	0.021, 0.117, 0.184, 0.345 0.655, 0.816, 0.883, 0.979
10	0.019, 0.076, 0.153, 0.217, 0.361 0.639, 0.783, 0.847, 0.924, 0.981

Because the log-linear method provides better accuracy than the tangential method for an equal number of measurements, it is recommended for velocity traverses in ducts of circular cross section. At the present time, the log-linear method is in general use in Britain (610,537).

Because of velocity gradient effects across the diameter of a pitot tube head, pitot tubes should have a diameter less than 1/30 the diameter of the duct when the allowed error is to be less than 1% (606).

4.3.2.2.2 Equal Area Division of Ducts of Rectangular Cross Section

The technique for dividing a rectangular duct into equal area zones is to divide the section into a number of geometrically similar rectangular zones and to measure the velocity at the centroid of each zone. The rules for the number of zones are more arbitrary than for circular ducts. As for

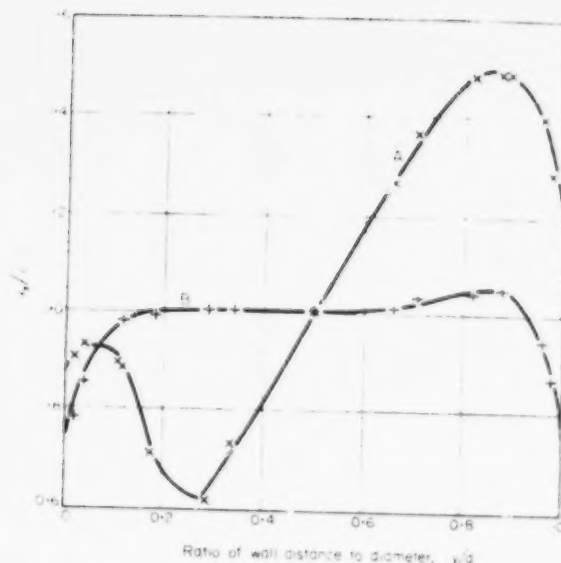


Figure 4-11. Types of Asymmetric Velocity Distribution in Pipes

circular ducts, the accuracy of the traverse will depend on the uniformity of the flow and the number of velocity measurements; however, it is a convention to increase the number of sampling points with duct size. The recommended number of test points are given in Table 4-6 as a function of the cross section area of the duct.

British Standards 1042 (615) recommends a division into at least 16 zones, with five velocity measurements in each corner zone, and three velocity measurements on each wall zone. The velocity in each zone is averaged before averaging the velocities over the duct. No zone should be greater than 36 inches², which means that more than 16 zones are necessary for ducts with cross sectional areas over 4 feet². The BSI Traverse plan is shown in Figure 4-12.

The National Engineering Laboratory (U.K.) has found that errors of 2% or more can occur for certain types of asymmetric flow distributions when the 16 part, 48 point traverse is used (606).

TABLE 4-6
TEST POINTS FOR RECTANGULAR DUCTS

A. Haaland (607)

Cross Section Area Square Feet	Number of Test Points
Less than 2	4
2 to 25	12
Greater than 25	20 or more

B. ASTM (614)

Inside Cross Sectional Area of Flue, ft ²	Minimum Number of Test Points
1* to 3	4
2< to 12	6 - 24
12<	More than 24

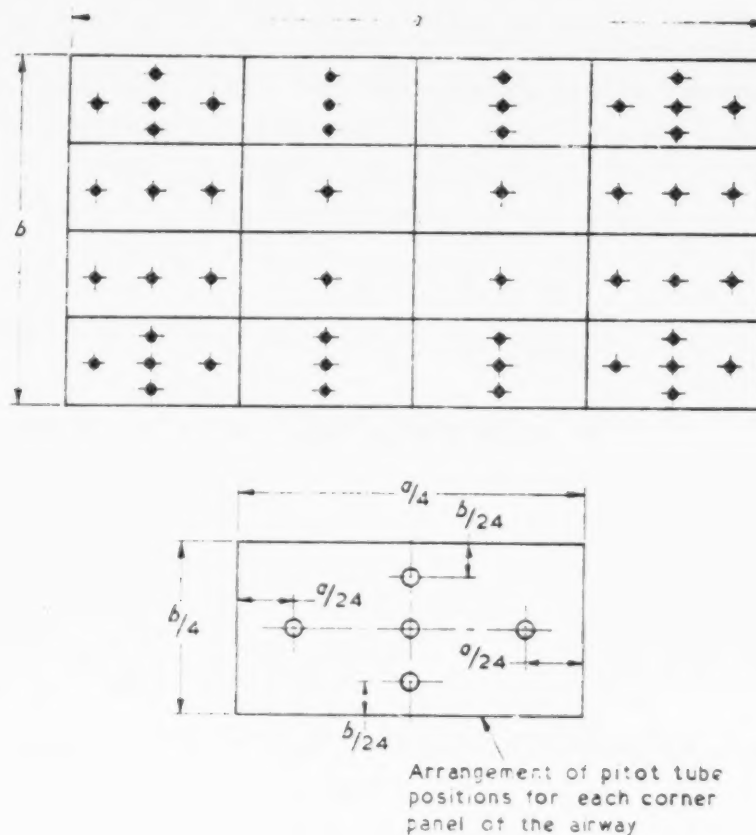


Figure 4-12. Traverse Plan for Rectangular Duct (610)

Because of velocity gradient effects across the diameter of the pitot tube head, it is usually recommended that the pitot tube diameter should be less than $1/30$ the shortest side. This value is probably based on the work done with circular ducts (see previous section).

4.3.2.2.3 Flow Variations During Traverse

Frequently the flue gas flow from a combustion source will not be constant during the time needed to traverse the duct. A reference pitot-static tube should then be placed in a fixed position in the duct to provide a reference velocity

pressure. With each reading of velocity pressure during the traverse, the reference pressure should be recorded. Each individual velocity pressure reading of the traverse is then reduced to the standard reference pressure P_s by multiplying it by the ratio P_s/P'_s , where P'_s is the reference pressure observed concurrently with that particular traverse velocity pressure.

4.3.2.3 Calculations of Volumetric Flow from Velocity Pressure

The relationship between velocity pressure and velocity is given by Equation (4). However, this equation is not very convenient for calculation. A more convenient form is Equation (6) below:

$$v = 2.90 \sqrt{\frac{29.92 T}{P GK}} \quad (6)$$

where

- v = gas velocity (feet/second)
- h = velocity pressure (inches of water)
- T = absolute temperature (degrees Rankine)
- P = absolute pressure of flue gas (inches of mercury)
- G = specific gravity of flue gas referred to that of air
- K = calibration factor of the pitot tube (for a standard type pitot-static tube K may be taken as unity)

The volumetric flow, if the gas temperature is constant across the duct, is found from Equations (5) and (6).

$$V = 2.90A \sqrt{\frac{29.92 T}{P GK}} \frac{1}{n} \sum \sqrt{h}$$

where the term $1/n \sum \sqrt{h}$ is the average of the square root of the velocity heads for an equal area traverse of n test points. V is the volumetric flow in feet³-second⁻¹, and A is the inside cross sectional area of the duct in feet².

4.3.3 Low Velocity Flow Measurement

4.3.3.1 Micromanometer - Pitot Tube

When measurements of gas velocities below about 15 feet per second and accuracies better than 1% are necessary, a micromanometer may be used to extend the gas velocity range of a standard pitot-static tube down to about 5 feet/second with an accuracy within 1%. The difficulty is that micromanometers (Figure 4-13) are more delicate than simple inclined manometers, and taking the velocity head readings is more tedious.

Electronic manometers are available which combine the sensitivity of micromanometers with the operational simplicity of the inclined manometer. A number of these instruments are briefly described below.

4.3.3.2 Electronic Micromanometers

The following companies manufacture electronic pressure measurement equipment (not complete listing):

1. MKS Instruments, Inc.
45 Middlesex Turnpike
Burlington, Mass.
2. Datametrics Division
CGS Scientific Corporation
127 Coolidge Hill Road
Watertown, Mass.
3. Datasciences Corporation
Instrument Systems Division
9601 Canoga Avenue
Chatsworth, California

The first two instruments use a pressure sensor that depends upon a change in capacitance due to a change in diaphragm geometry which is a function of the pressure differential across the diaphragm. The last instrument is similar except that the change in diaphragm geometry is detected by a change in reluctance.

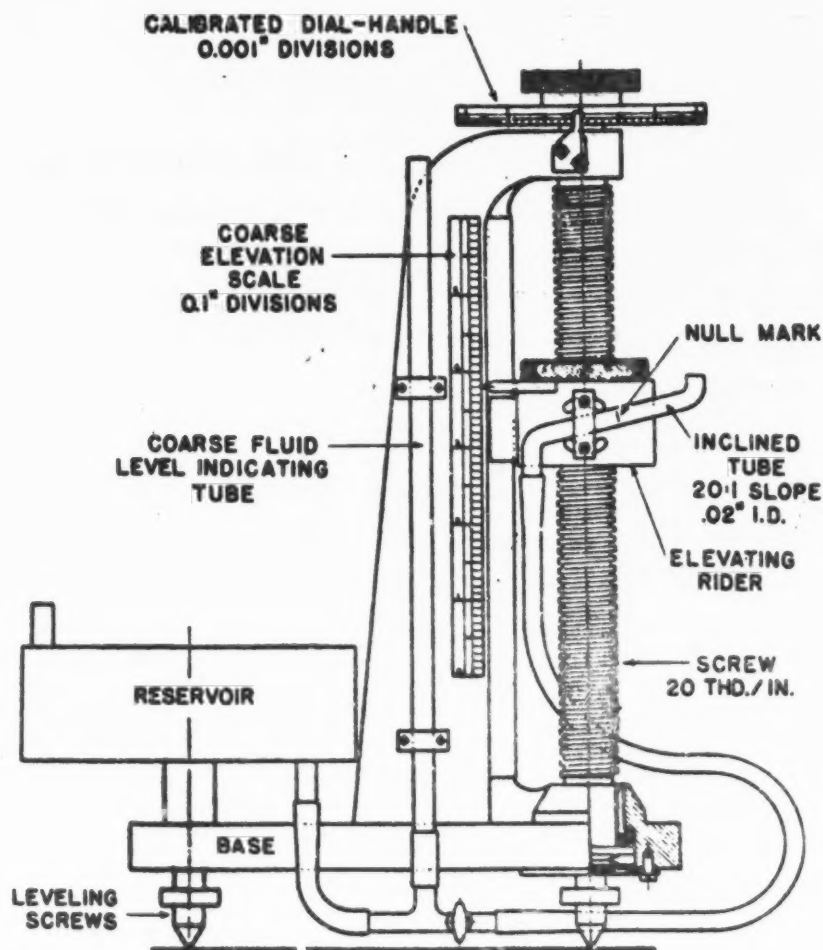


Figure 4-13. NACA Micromanometer

Both the MKS and CGS instruments have pressure ranges suitable for measurement of air velocities (at STP) from less than 2 to about 200 ft/sec using a standard pitot-static tube. The price range of these instruments is \$2,500 to about \$3,500 depending on digital or meter movement display.

The sensitivity of the Datasciences instrument does not offer much improvement over an inclined manometer. The most sensitive full scale deflection corresponds to an air velocity of about 20 ft/sec, which provides a useful low limit of about 6 ft/sec.

4.3.3.3 Hot-Wire Anemometer

For low velocity measurements in non-particulate laden gas streams, hot-wire anemometers may be used. Shielded hot-wire anemometers are commercially manufactured that will return to calibration when the shield is wiped clean of particles. H. Trissley & Co. Ltd. makes an instrument of this type which is accurate to within 0.5% for velocities of 5 down to less than 0.4 feet/second.

Hot-wire anemometers can be sensitive to the temperature of the gas streams; therefore, it is necessary to stay within the manufacturer's suggested temperature ranges.

4.3.3.4 Vane Anemometers

Vane anemometers are also employed to measure low speed flow. Figure 4-14 shows two configurations of vane anemometers. The dial of a vane anemometer is marked off in length units (usually feet) of air passing by the instrument. To measure velocity, it is necessary to take the time interval for a number of feet of air to pass the instrument and calculate the velocity.

Vane anemometers as shown above are suitable for measuring velocities in the range of about 1 to 10 feet/second. However, each instrument must be calibrated and the calibration should be frequently checked. The velocity measured must be corrected for the gas density by the following:

$$v = v_i \sqrt{\rho/\rho_0}$$

where v is the true velocity, v_i is the observed velocity, ρ is the density of the gas measured and ρ_0 is the density of the gas used for calibration.

For errors in volumetric flow less than 1%, this instrument should not be used in ducts smaller than about 8 times the diameter of the instrument (606). Traverses are made according to either the tangential rule or log-linear scale. Table 4-7 shows the

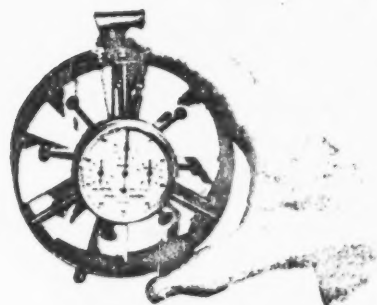


Figure 4-14. Vane Anemometers

limiting conditions for different sized anemometers in terms of the ratio of the duct, D , to the anemometer diameter, d .

4.3.3.5 Plate Orifice Meter

Volumetric flow measurements can be made, especially in small ducts, by measuring the differential static pressure across a flow constriction. The common types are plate orifices, shaped nozzles, and venturi tubes. The latter two types of constrictions are not readily applied to manual methods of source testing. The plate orifice, Figure 4-15, is a much simpler device and may be

TABLE 4-7
DIAMETER RATIOS FOR VANE ANEMOMETERS (606)

Number of Measuring Points Per Diameter	Distance of Nearest Point to Wall		Minimum D/d Ratio	
	Tangential Rule	Log-Linear Rule	Tangential Rule	Log-Linear Rule
4	0.067D	0.043D	7.5	11.6
6	0.043D	0.032D	11.5	15.6
8	0.032D	0.021D	15.4	23.8
10	0.026D	0.019D	19.8	26.3

adapted to small flues. There are two types of plate orifices, the standard and the calibrated. Standard orifices have been well investigated and when accurately constructed do not need calibration. The ASME standard orifice is reported to be in error less than 1% (611); while the British Standard orifice has a specified accuracy to within 1% in 95 out of 100 cases (606). Further details about these devices may be found in References 609 and 610. The standard orifices have the drawback that in flue gases their carefully machined sharp edged orifices will corrode and change performance characteristics.

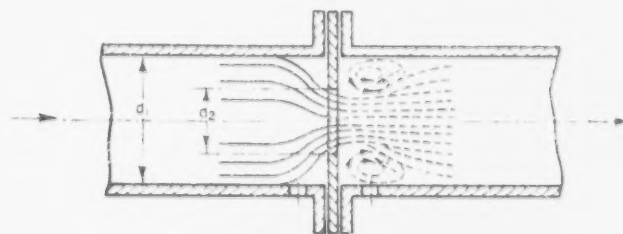


Figure 4-15. Flow Through a Plate Orifice

A more practical device is the calibrated orifice. This device is made by placing a thin orifice disc across a duct and calibrating the pressure differential against a standard technique such as a pitot traverse. It is convenient for measuring pulsing and time-changing flow because volumetric flow is presented in one reading.

4.3.4 Comparison of Volumetric Flow Measuring Methods

A comparison of volumetric flow measuring methods is presented in Table 4-8. A standard pitot-static tube traverse should be used wherever possible. When this is impossible and another method is selected, the instrument should be carefully calibrated if accurate results are expected.

4.3.5 Indirect Determinations of Volumetric Flow

4.3.5.1 Stoichiometric Method

An indirect technique to compute flue gas flow is by material balance. For these computations, it is necessary to know fuel composition, fuel flow rate, combustion air and exit particulate composition (to determine unburnt carbon content). This technique is based on the conservation of matter and the gas laws. The computational methods are aptly described in any standard stoichiometry textbook [e.g., Lewis and Radasch (612)]. Whereas such a technique certainly has a theoretical advantage in that no velocity probes are necessary, it does require accurate measurements of the input rates which may be difficult to obtain.

4.3.5.2 Dilution Technique

Dilution is an indirect technique that can be used to obtain volumetric flow through a duct. In this technique an inert tracer gas of known concentration is injected into the flue gas streams at a known flow rate. At a point far enough downstream for complete mixing of the tracer with the flue gas, the flue gas is sampled for the tracer gas concentration.

TABLE 4-8
COMPARISON OF VOLUMETRIC FLOW MEASURING METHODS

Measurement Method	Velocity Range	Applicable Flue Size (Characteristic Length)	Expected Error For Volumetric Flow (Well Developed Flow)	Remarks
Standard Pitot-	a, >15 ft/sec b, >5 ft/sec	30x Pitot Dia.	2%	a, Inclined manometer, b, Micromanometer, Pitot-static tubes are the practical standard for velocity measurements.
Staubscheibe Pitot Traverse	a, >12 ft/sec	Same as Above	----	a, See above Accuracy depends on calibration
Hot-Wire Anemometer	>0.4 ft/sec	Several Times Larger Than Probe Size	2%	Clean gas stream required, fast response time, requires frequent calibration low gas temperature
Vane Anemometer	>1 ft/sec <10 ft/sec	8x Diameter of Anemometer	----	Frequent calibration & clean gas, stream required
Standard Plate Orifice	----	Practically all	~1%	No calibration needed, short lifetime in flue gases, must be constructed for particular flue
Calibrated Plate Orifice	----	Same as Above	----	Accuracy depends on calibrations, more rugged than standard plate orifice, convenient where flow cycles, introduces pressure drop in flow system

The volumetric flow in the duct is then calculated from the equation:

$$V = q_i (C_i/C_s - 1)$$

where V is the flue gas volumetric flow, q_i is the tracer gas injection flow rate, C_i is the tracer gas concentration at the injection point and C_s is the tracer gas concentration at the sampling point.

To utilize this technique, C_s must be measured accurately, since to determine V within 1%, C_s must be measured within 1%.

5. SAMPLING METHODS FOR SULFUR OXIDES

5.1 Introduction

The key to satisfactory analysis is collection of a representative sample, selection of the proper probe, collecting medium, and analytical method. Oxidation of $\text{SO}_2 \rightarrow \text{SO}_3$ (catalytically) is a factor to be considered both in the probe and in the collecting medium employed. For example, if the probe is heated to very high temperatures, catalytic oxidation of SO_2 can occur (526). Condensation of H_2SO_4 and water in the probe can lead to low SO_3 (and SO_2) values. Interferences with the analytical method may be avoided by the proper choice of collecting medium. Thus, the sampling system (probe, collecting medium, analytical method, etc.) has to be considered as a whole in order to obtain truly precise and accurate results. A complete sampling system for the sulfur oxides designed during this program is given in Appendix 4.

These factors are discussed in detail below.

5.2 Probes

The material of construction is a significant factor in selecting probe components. The selection of a sampling probe must include consideration of the mechanical properties of the equipment as a function of the temperature range and chemical environment to be encountered. Other factors involved in the selection of flue gas probes such as cost, frequency of maintenance, accessibility, etc., have been mentioned by Dixon (505). The British Standards Institution (379) and ASME (502) describe probes, collecting equipment and methods commonly used for flue gas sampling. A water-cooled multipoint probe designed by Chojnowski (500) can be used for taking three simultaneous gaseous samples.

Probes may be divided into two classes, viz., simple* and temperature-controlled. Provision must be made for a preliminary

* A simple probe is not temperature controlled.

filter, (quartz or pyrex wool) to remove combustion generated particulates which may interfere with the analysis or change the composition of the flue gas. Typical power plant sampling points are described in Table 5-1. (Also see Figure 4-4.) Typical probes are described in more detail in the following sections.

TABLE 5-1
TYPICAL POWER PLANT SAMPLING POINTS

Sampling Location	Temperature Range (°F)	Purpose
In furnace above burner*	2000-3000	(More important for NO _x process control studies)
Before air heater	700-800	For checking combustion control
Exit of air heater	300-400	Emission inventory or heat balance

* Not in mission of present program

5.2.1 Simple Probes

A simple probe may be a stainless steel tube (170) or a stainless steel tube with a quartz or pyrex insert (76). The latter has been used with some success where the flue gas temperature is in the vicinity of 500°F (76). The problem commonly encountered in sampling with an unheated probe is that cooling of the flue gas in the probe and/or sampling lines may lead to condensation. For example, for an SO₃ concentration of 10 ppm, the dewpoint of the flue gas is 270°F (Figure 5-1). In a series of tests at a coal-fired power plant, up to 50% of the total SO₃ was found in the probe and sampling lines (527). Therefore, the probe and sampling line have to be

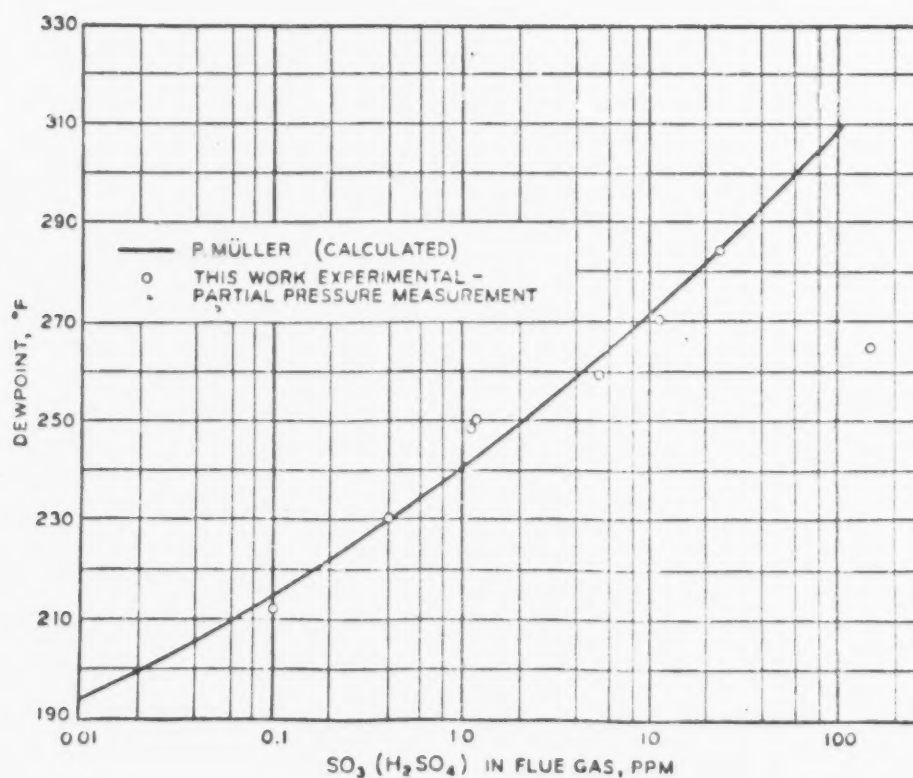


Figure 5-1. Sulfuric Acid Dewpoint as a Function of SO₃ Concentration (502)

quantitatively washed into the collection vessel. As a result of this cumbersome procedure, the use of this probe is not recommended.

5.2.2 Temperature Controlled Probes

5.2.2.1 Heated

Most of the sampling in power plants is done in the duct work after the air heater where the temperature is in the vicinity of 350°F. For this application, the heated probe described by ASME (502), BSI (381) (Figure 5-2) is most suitable (80,81,119,217, 165,221,218,160,215,207). In operation, the probe (quartz or pyrex tube inside a stainless steel case) is electrically heated to a temperature (500-600°F) well above the acid dewpoint. Heating of the sampling lines from the probe to the collector is generally necessary to prevent condensation. A heated probe is recommended for flue gas temperatures less than 800°F.

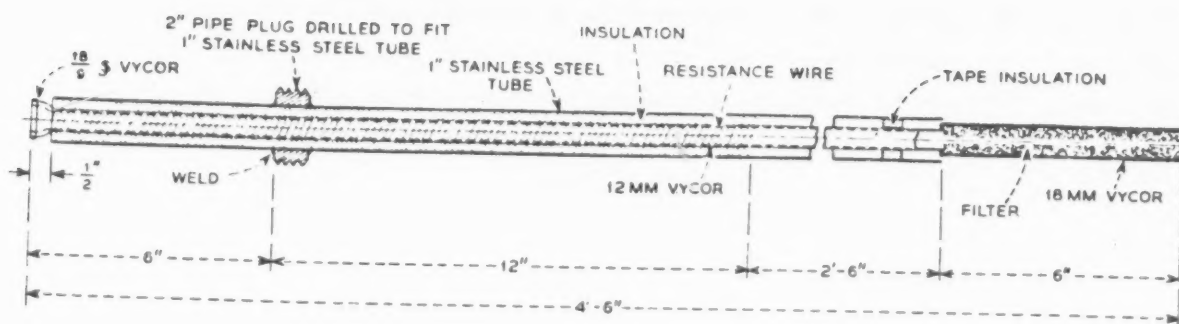
5.2.2.2 Water-Cooled

When sampling at temperatures above 800°F, several changes in the probe design are needed. Pyrex inserts have to be replaced with quartz and the probe has to be cooled to approximately 600-700°F to prevent changes in the composition of the flue gas. Water cooled probes (Figure 5-2) with quartz inserts have been used by B&W (425), BSI, and ASME. These water cooled probes have been used for taking NO_x samples in the furnace where temperatures approach 2500°F. (This problem is not considered further in this program, since it exceeds the temperature range of interest.)

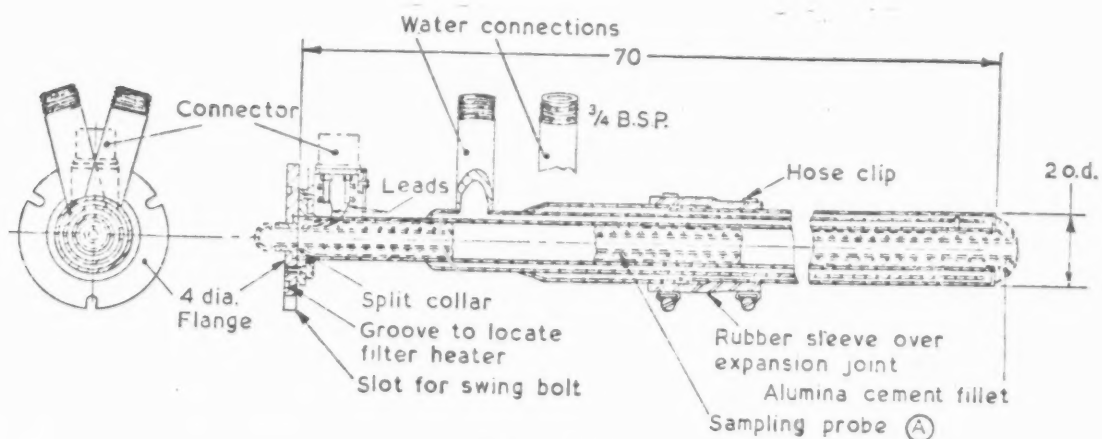
5.3 Collection Methods for SO₃

5.3.1 Introduction

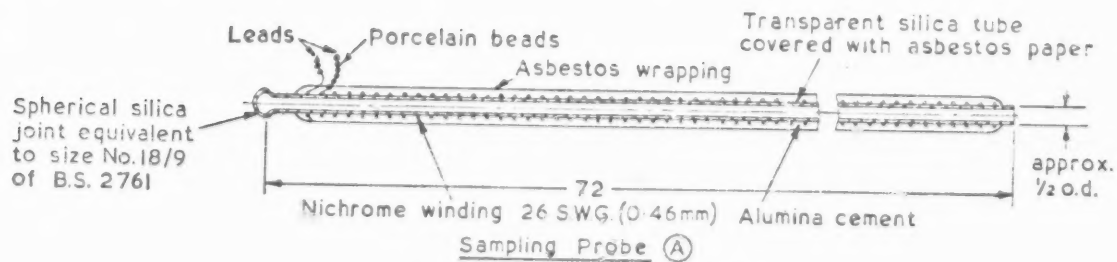
Most literature references on collection methods for SO₃ deal with concentrations less than 50 ppm, characteristic



STAINLESS STEEL VYCOR SAMPLING PROBE



Water Jacket



Heated probe unit with water-cooled jacket

Figure 5-2. Heated and Cooled Probes

of fossil fuel plants. These measurements have been made for diagnostic purposes (i.e., corrosion control, etc.) since the SO_3 concentration is only about 1-2% of the total sulfur oxides emitted. This low SO_3 concentration limits the collection techniques to those which concentrate the sample, e.g., absorption, rather than grab sampling techniques. A summary of general sampling methods for gaseous pollutants is given in Table 5-2. The other principal SO_3 sources are sulfuric acid plants and smelters. Techniques used for sulfuric acid plants have been described by MCA (95) and are generally those developed for fossil fuel combustion. No new collection techniques appear to have been developed for the smelting industry (496).

The major problem in quantitative collection of SO_3 in power plant effluents is that SO_2 , present in a large excess, is easily oxidized, leading to high SO_3 values and/or poor precision and accuracy. Most collection methods for the sulfur oxides have been based upon physical separation of SO_2 and SO_3 (by differential absorption) to reduce the magnitude of the oxidation problem. Techniques in which both oxides are collected without separation (such as absorption in caustic solution) have not been widely used since accuracy is generally poor.

SO_3 collection techniques may be divided by approach into two different classes: absorption and condensation methods. The former depend on the solubility of H_2SO_4 in aqueous solutions. Inhibitors, such as alcohols, have generally been added to prevent the oxidation of dissolved SO_2 . Condensation methods depend upon cooling of the flue gas (controlled or uncontrolled) to a temperature where H_2SO_4 aerosol is formed and subsequent collection on a sintered glass frit or filter paper.

In principle, solid adsorbents, reactive or unreactive, may be used for collection of SO_3 . We have found no references to analyses of effluents for SO_3 utilizing this technique.*

* This approach may indeed be useful for SO_x and/or NO_x measurements, but we do not recommend attempts to develop such a technique for SO_3 .

TABLE 5-2
COMPARATIVE SUMMARY OF SAMPLING DEVICES (542)

TYPE OF CONTAMINANT	PRINCIPLE OF METHOD	INSTRUMENTS	APPLICATION	METHOD OF QUANTITATION	SKILL IN OPERATION	SKILL IN QUANTITATION	REMARKS
Gaseous	Absorption	Bubbler trains		Chemical Analysis	Some		Efficient for collection of reactive gases. Efficiency low for fine particulate matter and gases of low or slow solubility. Simple commercially available equipment.
	Absorption	Spray collector		Chemical Analysis	Considerable		Efficiency low for gases of low or slow solubility. More efficient when filters for particulate matter are used. Limiting factor is rate of volume of liquid used. Increasing sensitivity of test. Spray losses should be considered. Equipment not commercially available.
	Absorption	Tubes of cartridges filled with charcoal, silica or alumina gel.	General Atmospheres	Weight Chemical Analysis	Considerable	Considerable for Trace Quantities	Highly efficient for collection of wide variety of gases reactive and non-reactive. Chemical analysis requires desorption under pre-tested conditions. Equipment must be constructed to meet test conditions. Not ordinarily commercially available.
	Condensation	Freeze-out	Ducts Stacks	Chemical Analysis	Considerable	Less for Gaseous Amounts	Highly efficient for relatively non-volatile vaporized liquids. Requires low temperature refrigeration liquid such as dry ice. Apparatus may be assembled from commercially available components.
	Absorption and mechanical retention	Bottle collection	(Low concentrations)	Chemical Analysis	Some		Efficient for gases of slow solubility. Quick and convenient method. No power source needed at sampling position. Gas volumes limited to size of available containers. Equipment readily available.
		Plastic bag collection		Chemical Analysis	Little		Useful as light weight large volume container. For trace quantities wall adsorption must be considered and adsorbed gases removed by solution in reagent. Not recommended for particulate matter. Not commercially available.

Since SO_3 is collected as H_2SO_4 , analysis may be performed by methods specific for sulfate or the acid content may be determined by neutralization methods. These methods are discussed in detail in Section 5.4.

5.3.2 Absorption in a Liquid

5.3.2.1 80% Isopropanol

Alyea and Backstrom (306) found that several higher alcohols (isopropyl, sec-butyl and benzyl) prevented the oxidation of dissolved SO_2 . Flint (131) selected isopropanol because it is miscible with water, its inhibiting action extends over long periods of time, and it may be employed as a constant boiling mixture. An additional advantage is that the solubility of SO_2 in IPA solutions is considerably lower than in distilled water.

The collection of SO_3 from power plant flue gases by absorption in 80% IPA is the most widely used collection method (160,215,218,221,263,78,516,425,52,145,300,527). The IPA solution is used as a prescrubber for SO_3 , and SO_2 is collected in H_2O_2 or another absorbing solution. A drawback of the technique is that the SO_2 dissolved in the solution must be removed immediately by purging to prevent oxidation of sulfite ion to sulfate.

Flint (131) determined the collection efficiency for H_2SO_4 aerosol in 80% IPA. He found that the collection is quantitative with two collectors and a filter all in series (Table 5-3), although the efficiency of each of the three elements is quite low. Although a number of different collection devices have been used, little data on SO_3 collection efficiency has appeared. Corbett (160,215) and others (218,221) use Flint's apparatus (Figure 5-3a); Seidman (78) uses three lamp sulfur absorbers in series, while others use midget bubblers (559,516,425,527).

TABLE 5-3
COLLECTION EFFICIENCY OF SO₃ IN 80% IPA (131)

Test	1	2	3	4	5	Average
% Bubbler 1	29	40	47	44	48	42
% Bubbler 2	50	46	42	47	45	46
% Filter	<u>18</u>	<u>13</u>	<u>12</u>	<u>9</u>	<u>7</u>	<u>12</u>
Total	97	99	101	100	100	100

Juntgen (530) reported a "drastic" decrease in the collection efficiency of Flint's Apparatus at ~1 lpm. Since this work was performed by comparison to another collection device, the absolute efficiency was not determined.

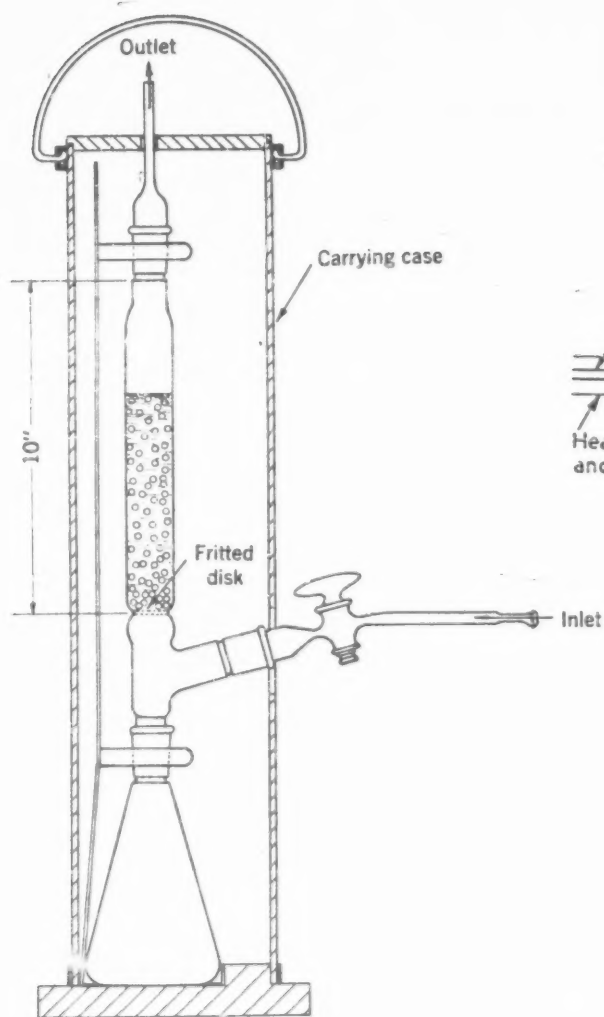
As a result of the importance of IPA absorption methods and the scarcity of absorption efficiency determinations, we have carried out laboratory measurements for several important collectors as a function of flow rate.*

SO₃ collection efficiencies were determined in a simulated combustion effluent (3% O₂, ~10% H₂O, 87% N₂) maintained at flue temperatures (300°F) up to the collectors. The collection devices evaluated were:

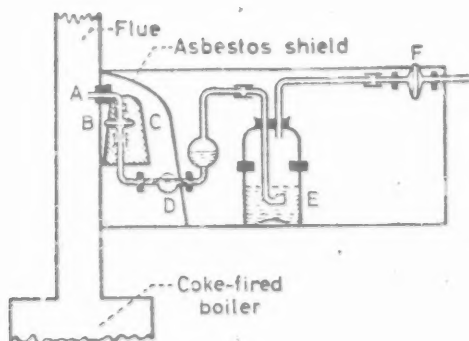
- a. midget impingers
- b. midget bubblers
- c. lamp sulfur absorbers

These devices were charged with 80% isopropanol-20% water and immersed in an ice bath. Known volumes of the

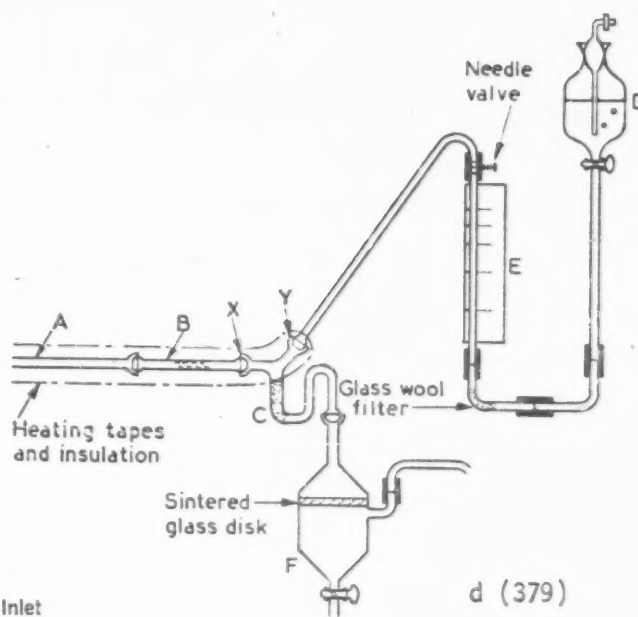
*The delivery system is described in Appendix 5 of this report.



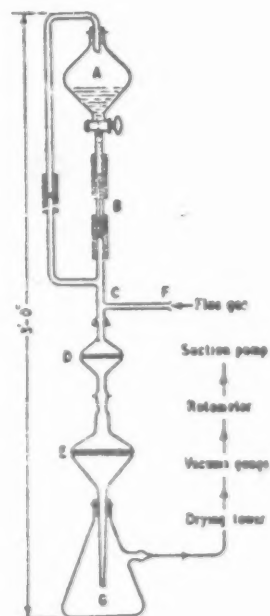
b(76)



a(218)



d (379)



c(310)

Figure 5-3. Collection Devices for SO_3

simulated flue gas were drawn through the collectors using critical orifices as metering devices. The total sample volume collected was 15 liters for the midget impingers and bubblers and 30 liters for the lamp sulfur absorbers. The SO_3 collected was analyzed as sulfate by the barium chloranilate colorimetric procedure. The results for the three devices tested are described below:

Midget Impingers - The collection system under test was made of two midget impingers in series followed by a high efficiency (millipore) glass fiber aerosol filter. Each impinger was filled with 15 cc of the 80% isopropanol-20% water solution. Collection efficiency was obtained as a function of flow rate, by determination of the fraction of the total SO_3 (impingers + filter) in the first and in both impingers. The results obtained are summarized in Table 5-4.

Within the precision of the results, a high and constant (90%) collection efficiency is obtained for the primary impinger in the range 0.5-3.0 lpm. Within this range the observed efficiency of two series impingers is a constant 95%, significantly below quantitative collection, however.

The last column of Table 5-4 is the collection efficiency for two impingers calculated on the basis of the measured efficiency of the primary impinger taken to be constant at a given flow rate. Comparison of observed efficiencies for two series impingers to the calculated values clearly shows that the effective efficiency of the second impinger has fallen to about 50% (in the range 0.5-3.0 lpm). The most direct interpretation of these results is that the collection efficiency of the midget impinger decreases as the concentration decreases. However, examination of the very wide concentration ranges included for a given mean (0.5 and 3.0 lpm, for example) does not show pronounced concentration dependence. (See also following section on concentration dependence.)

TABLE 5-4
COLLECTION EFFICIENCY OF MIDGET IMPINGERS FOR SO₃^a

Flow Rate LPM	Number of Replicates	Mean SO ₃ ^b Conc. ppm	Collection Efficiency, %		
			Primary ^c	Both ^c	Calc. ^d
0.5	3	208 ± 140	90 ± 2	94 ± 2	99
1.0	3	220 ± 20	87 ± 3	93 ± 3	98
3.0	2	170 ± 80	94 ± 2	97 ± 1	99.6
5.0	3	93 ± 20	70 ± 5	84 ± 2	91

a. 15 liter sample collected in 15 ml 80% IPA at 0°C

b. mean SO₃ concentration for all runs = 173 ppm

c. ranges are average deviations

d. calculated on basis of constant efficiency measured for primary impinger at given flow rate

At the highest flow rate (5 lpm) a significant decrease in the collection efficiency of the impinger is observed. The collection efficiency of the second impinger remains, however, at only 50%! It is difficult to reconcile this result with a simple interpretation of the low efficiency of the second impinger (e.g., a non-wetted fraction of the original aerosol). However, too much emphasis should not be placed on this single value, since it was obtained in the reduced efficiency range, and other factors may come into play. Midget bubblers do not show this behavior (see below).

Midget Bubblers - The collection system under test was made of two midget bubblers in series, again followed by a high efficiency filter. The bubblers were each charged with 15 ml of 80% IPA solution. The observed collection efficiencies are given in Table 5-5 as a function of flow rate.

The collection efficiencies for a single bubbler are significantly lower than for a single midget impinger at all flow rates.* In the range 0.5-1.0 lpm, however, the observed efficiencies of two bubblers in series are the same as for two series impingers, within the precision of the results. In striking contrast to the impinger results, the efficiency of both bubblers at a given flow rate remains constant over the entire flow range, although the efficiency for a single bubbler drops from 73% to 35% over the range measured.

Lamp Sulfur Absorbers - The lamp sulfur absorbers tested were of the NAPCA design, which includes a spray tower. The absorber (but not the spray tower), was immersed in an ice bath with 30 ml IPA solution in the absorber and 10 ml in the spray tower. A high efficiency filter was placed downstream to complete the system under test. Analyses were performed of the combined absorber and

* This result must be qualified by noting that the mean SO_2 concentration is less than half the mean concentration for the impinger tests.

TABLE 5-5
COLLECTION EFFICIENCY OF MIDGET BUBBLERS FOR SO₃^a

Flow Rate LPM	Number of Replicates	Mean SO ₃ ^{b,c} Conc. ppm	Collection Efficiency, %		
			Primary ^c	Both ^c (Exp)	Both ^d (Exp)
0.5	4	100 ± 30	73 ± 6	94 ± 2	93
1.0	2	75 ± 25	73 ± 5	93 ± 2	93
3.0	5	49 ± 20	58 ± 6	83 ± 10	82
5.0	2	29 ± 8	35 ± 5	60 ± 8	58

a. 15 liter sample collected in 15 ml 80% IPA at 0°C

b. mean SO₃ concentration for all runs = 66 ppm

c. ranges are average deviations

d. calculated on basis of constant efficiency measured for primary bubbler at given flow rate

spray tower solutions and separately of the filter to obtain collection efficiencies. The results obtained are shown in Table 5-6 as a function of flow rate.

TABLE 5-6
COLLECTION EFFICIENCY OF LAMP SULFUR ABSORBER FOR SO_3^a

Flow Rate LPM	Number of Replicates	Mean SO_3 Conc. ppm ^{b,c}	Collection ^c Efficiency, %
1	2	130 ± 100	95 ± 5
3	3	120 ± 60	96 ± 2
5	2	90 ± 30	95 ± 2

- a. 30 liter sample collected in 30 ml 80% IPA at 0°C in absorber and 10ml 80% IPA at ambient in spray tower
b. mean SO_3 concentration for all runs = 114 ppm
c. ranges are average deviations

The collection efficiency of the lamp sulfur absorber is constant over the range 1-5 lpm and equal to the best values obtained for two series impingers or bubblers over the more limited flow ranges for efficient collection which apply to those devices.

Summary of Collection Efficiency Results - A comparison of the observed collection efficiencies for the three systems tested is given in Figure 5-4 as a function of flow rate. Maximum efficiency of 95% is observed for all trains (excluding the filter). The (two) midget bubblers are most sensitive to loss of efficiency with increasing flow rate. The collection efficiency of the lamp sulfur absorber is, however, constant in the range 1-5 lpm.

Concentration Dependence of the Collection Efficiency of Midget Impingers - We have investigated the collection

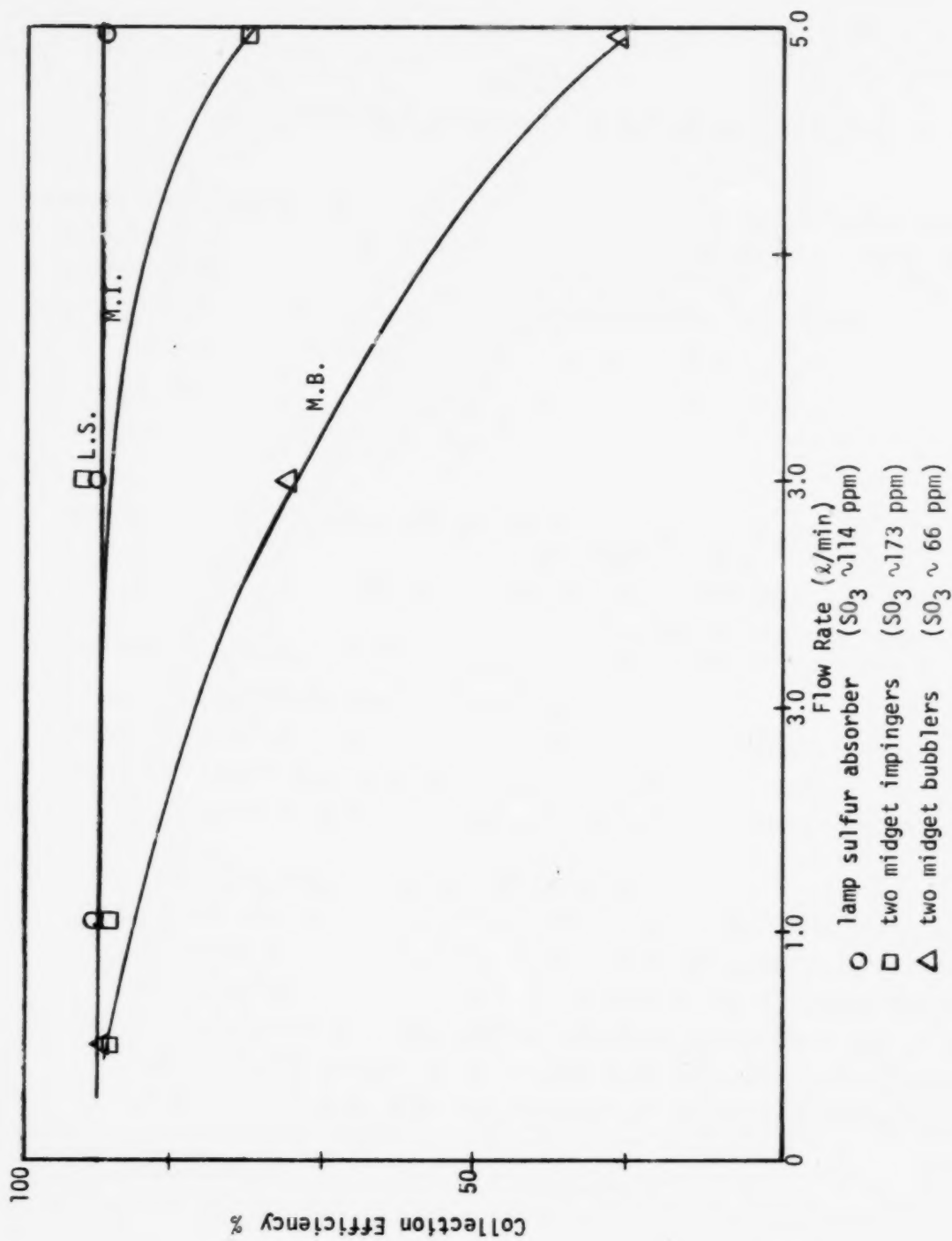


Figure 5-4. Collection Efficiencies for SO₃ as a Function of Flow Rate

efficiency of midjet impingers as a function of SO_3 concentration at 5 lpm (where collection efficiency for two impingers has dropped from the maximum value). The results obtained are shown in Figure 5-5. The upper straight line represents the efficiency for two series impingers. The data have been fitted by simple linear regression analysis. The slope is significantly different from zero at the 85% confidence level but suggests that the concentration dependence (at 5 lpm) is relatively small.

The lower curve of Figure 5-5 for a single impinger is quite different from the two series impinger results and shows a rapid decrease in efficiency with decreasing concentration. Since there is considerable scatter in the data at 30 ppm SO_3 , the reliability of the results may be questioned. Taken at face value, however, these results imply considerably increased efficiency at low concentrations for the second impinger compared to the first. This is the direct reverse of the behavior observed at high concentrations ($\text{SO}_3 \approx 170$ ppm).

Conclusions - Collection efficiencies are less than quantitative for all conditions investigated if a final filter is not used. Further work should be conducted at SO_3 concentrations in the 10-20 ppm range to determine collection efficiencies as a function of flow rate.

5.3.2.2 Boiling Water

The principle of this method is that SO_2 and SO_3 can be separated by their differential solubilities in boiling water (337); SO_2 is essentially insoluble, but SO_3 is quite soluble in boiling water. No data are available for this promising collection method.

5.3.2.3 Aqueous Sodium Hydroxide

SO_2 and SO_3 are collected together in a device such as that illustrated in Figure 5-3b. The collection

Collection Efficiency, % = $74 + 0.127 (\text{Conc. SO}_3, \text{ppm})$
(two impingers)

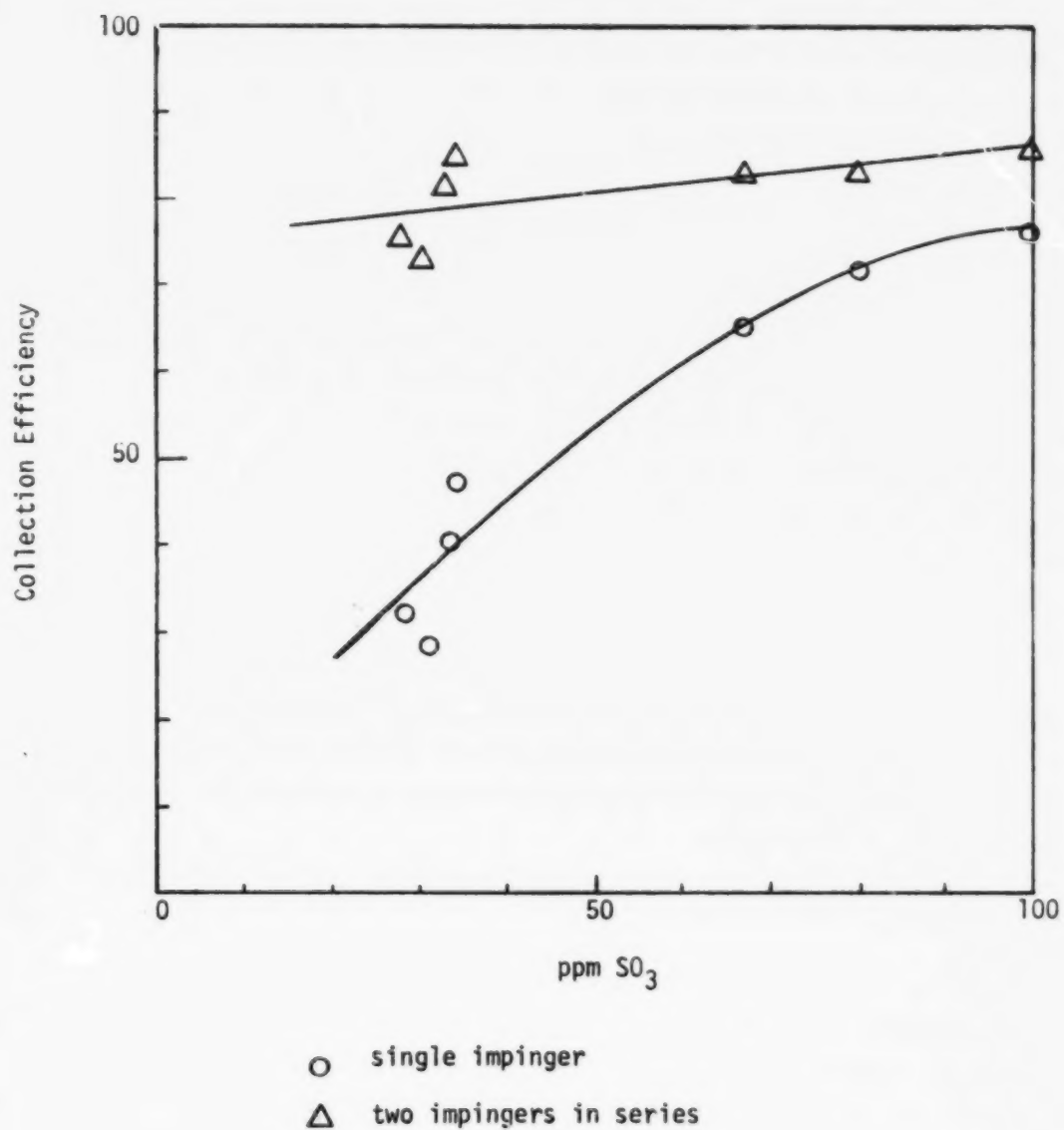


Figure 5-5. Collection Efficiency of Midget Impingers as a Function of Concentration (Sampling Rate = 5 l/min)

technique is susceptible to both the oxidation problem and to many interferences in subsequent analysis (see following sections). Many inhibitors such as benzaldehyde, mannitol, furfural, and glycerol, have been tried in an attempt to prevent oxidation of SO_2 , but none of these appears to have solved this problem. In Table 5-7 we compare results of SO_3 measurements obtained by collection in caustic (NaOH) to both 80% isopropanol and distilled water scrubbing solutions. In each case the caustic scrubbing results are approximately 50% higher than the others. These data indicate that sulfite oxidation may be a major problem in caustic scrubbing. No data on the collection efficiency of SO_3 in NaOH solutions has been located.

5.3.2.4 Distilled Water

Gillham's (161) results indicate that when SO_2 is bubbled through aqueous acid, over a 24-hour period the fraction oxidized is approximately 25%. If the oxidation rate is linear it would amount to 1%/hr. which is significant. If $\text{SO}_3/\text{SO}_x = .01$, the apparent SO_3 content of a 15-minute sample would be increased by 25%. This method has not been widely used for collection of SO_3 in the presence of SO_2 since the sulfite oxidation contribution cannot be adequately calculated (as Gillham suggests). The system is also not specific since the solubility of SO_2 in water is high (requiring another correction for most analytical methods). This technique could be used to collect SO_3 where little SO_2 is present (e.g., a Monsanto Cat-ox stream) since SO_3 can be collected quantitatively (161, 528) in distilled water.

5.3.3 Condensation Methods

Condensation methods depend upon the presence of water vapor to form H_2SO_4 mist by reaction with SO_3 and are, therefore, limited to a moist stream such as a combustion effluent. In the controlled, as well as the uncontrolled condensation methods, SO_2 and SO_3 are collected separately.

TABLE 5-7
COMPARISON OF SO₃ ANALYSES AS A FUNCTION OF COLLECTION METHOD

	ppm SO ₃ 80% IPA Collection* (548)	ppm SO ₃ Caustic Collection** (NaOH) (548)
Inlet	8	16
Outlet	11	16
Inlet	14	16
Outlet	13	14
Inlet	7	18
Outlet	12	17
Inlet	8	12
Outlet	<u>13</u>	<u>19</u>
Average	11	16

	ppm SO ₃ Distilled Water Collection (161)	ppm SO ₃ Caustic Collection (161)
	4	8
	10	9
	6	13
	<u>5</u>	<u>8</u>
Average	6	9.5

* Determined by titration with Ba(ClO₄)₂ and thorin indicator

** Determined by the Berk and Burdick method

5.3.3.1 Controlled Condensation

Johnstone (529) was perhaps the first to recognize that the dewpoint of the flue gas was a function of the SO_3 concentration. Although a considerable amount of work had been done on the relation of the flue gas dewpoint to the SO_3 concentration, it wasn't until the theoretical work of Muller (495) and the experimental work of Lisle and Sensenbaugh (80) that this was clearly established. The correlation of the experimental results with calculation is shown in Figure 5-1. By reducing the temperature below 200°F , one can remove the SO_3 (as H_2SO_4) from a (wet) flue gas essentially quantitatively.

It is well known that when air containing SO_3 and moisture is rapidly cooled, a sulfuric acid aerosol is formed. Goodeve (506) and Kerrigan and Snajberk (509) have shown that H_2SO_4 mist can be collected quantitatively with a filter. Using this principle, Knol (511,403), Kantor (508), Hissink (119,415) and others have used controlled condensation of flue gas (at $60\text{-}90^\circ\text{C}$) to form H_2SO_4 aerosol and collected it on a filter.*

Goksoyr and Ross (81) collected the sulfuric mist on a sintered glass frit (Figure 5-6). This technique has gained favor recently (35,80,127,119,55,103). The major advantage of controlled condensation is that SO_3 is quantitatively condensed at a temperature ($60\text{-}90^\circ\text{C}$) above the water dewpoint. SO_2 is therefore not retained in the SO_3 collector and the two species are easily separated, essentially eliminating the problem of SO_2 oxidation.

A number of investigators have determined that quantitative collection of sulfuric acid mist is obtained by the controlled condensation technique (80,81,119,415). Typical results of controlled condensation collection are given in Table 5-8.

*A modification of this technique described by Schneider (104,264) uses a tube of sodium chloride to filter the H_2SO_4 aerosol.

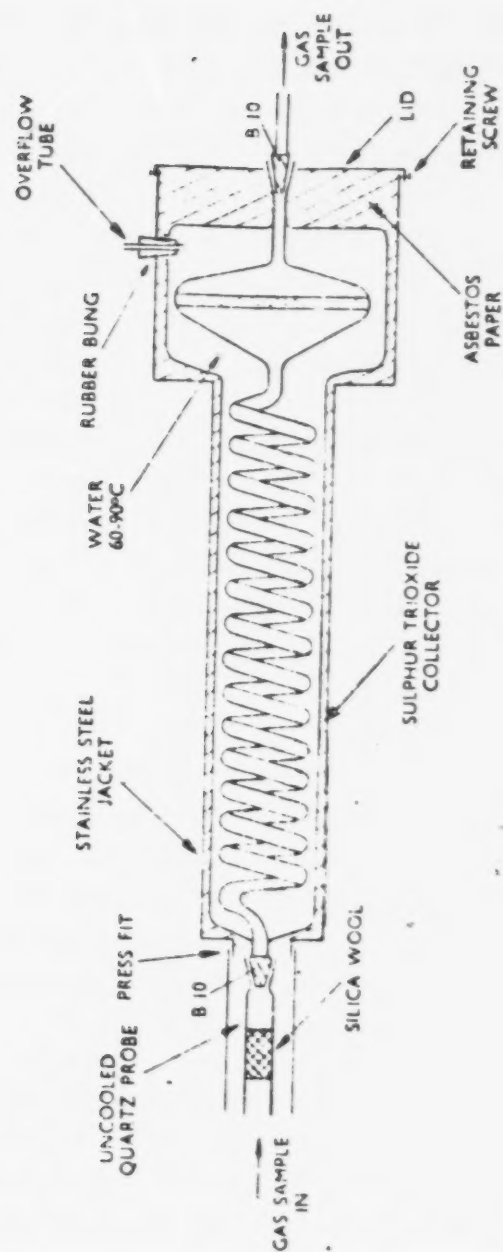


Figure 5-6. SO_3 Controlled Condensation Apparatus

TABLE 5-8
SO₃ COLLECTION EFFICIENCY USING
CONTROLLED CONDENSATION (415)

Experiment	SO ₂			SO ₃			Remarks
	(a) in gas mixture	(b) determined	100 b	(c) in gas mixture	(d) determined	100 d	
	p.p.m.		a	p.p.m.		c	
A	47	45	97	693	713	103	no dust filter in the apparatus.
B	44	44	101*	732	721	98	
C	10.0	10.6	106	733	735	100	
D	9.4	9.6	102	690	693	100	
E	37	39	104	695	699	100	dust filter in position.
F	39	41	105	701	724	103	
G	10.8	11.3	105	838	853	102	
H	9.4	9.4	100	717	771	107	
I	4.8	4.8	99*	638	661	103	
J	4.7	4.7	101*	702	741	105	
K	3.0	2.8	93	899	900	100	
L	0.98	0.94	96	750	762	102	
M	42	44	104	760	760	100	temp. before filter e 270 C; behind filter 50 C.
N	44	44	101*	732	721	98	" " " 300 C; " " 50 C.
O	44	41	93	737	725	98	" " " 250 C; " " 80 C.
P	39	18	47	716	625	87	" " " 250 C; " " 140 C.
Q	40	37	91	1128	1152	102	with filter paper temp. near filter 130 C.
R	42	42	100	1104	992	90	" " " " 90 C.
S	56	57	102	1560	1660	106	with flue gas in apparatus; G4 filter.
T	15	15	100	1700	1770	103	with flue gas; filter paper.
U	12	12	100	1405	1430	102	

5.3.3.2 Uncontrolled Condensation

This method is a modification (379,217,165,178, 310,170) of Flint's technique (absorption in 80% IPA). The collection vessel may consist of a double sintered glass frit (Figure 5-3c) or a single frit such as that adopted by the British Standards Institute (Figure 5-3d). The stack gas is passed into a vessel at ambient temperature. The resulting (uncontrolled) cooling produces H_2SO_4 mist which is collected on a glass frit. H_2SO_4 is constantly removed from the frit by a flowing stream of 80% IPA-20% water. The major difficulty is that water condenses with the H_2SO_4 mist. Since SO_2 is very soluble in water, the problem of oxidation of SO_2 remains. This collection technique is, thus, not basically different from the 80% IPA absorption method previously discussed. The complexity and fragility of the required apparatus are a definite drawback in field sampling. No data on the absolute efficiency have been found.

5.3.3.3 Dewpoint Method

This technique provides at best an estimate of the SO_3 concentration. The probe for collection of H_2SO_4 (Figure 5-7) is inserted into the stack. Compressed air is passed through the probe to establish a temperature gradient to initiate H_2SO_4 aerosol formation on the surface. The temperature is measured at various points along the probe. After a known time has elapsed, the probe is removed and each section washed and titrated with standard base. From the analysis and temperature profile, the dewpoint, and therefore the SO_3 concentration, can be determined.

The British Standards Institute gives the reproducibility of the dewpoint temperature as $\pm 6^\circ\text{C}$. At 10 ppm SO_3 the precision is ± 7 ppm and the coefficient of variation about 70%. Clearly, this is a very imprecise method and will not be further considered.

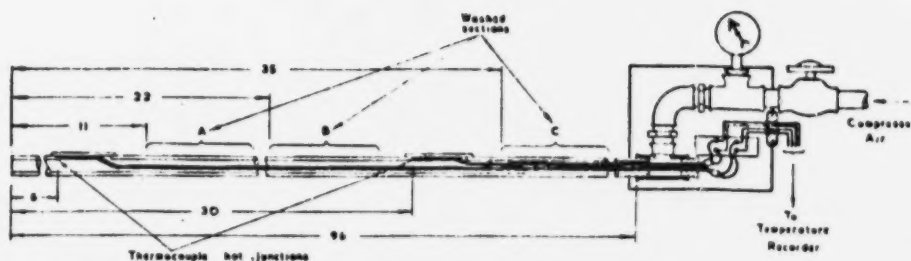


Figure 5-7. Acid-Deposition Probe (Part Section) (531)

5.4 Collection Methods for SO₂

5.4.1 Introduction

The literature search conducted for SO₂ collection methods has included examination of all areas where analysis of gaseous sulfur compounds is of significance. In addition to fossil fuel combustion sources, relevant sampling techniques have been employed in ambient (air) analysis and in the petroleum, chemical, smelting, and pulp and paper industries. Although the objectives of a number of sampling techniques developed for purposes other than heat and power generation may be different from those required for fossil fuel sources, we have attempted to make our discussion complete, in order to indicate possible areas for future development.

In the following sections, we describe aqueous and solid absorbents which have been utilized in the past or which appear promising as a result of peripheral application. We do not, however, attempt to "invent" new collection methods for which the potential appears low. There is, thus, for example, no discussion of organic liquids which have recently been examined for possible application to flue gas scrubbing (510).

The concluding section discusses the adaptation of ambient methods by dilution techniques.

5.4.2 Aqueous Absorbents

5.4.2.1 Hydrogen Peroxide

A. Description of Method

This has been the most widely used collection method for SO_2 (78, 80, 81, 125, 119, 131, 218, 35, 221, 403, 516, 521).

The sample, after removal of SO_3 in a prescrubber, is bubbled through a solution of hydrogen peroxide which oxidizes SO_2 to sulfuric acid. The resulting H_2SO_4 has been determined by a variety of methods, either specific for sulfate or by titration to a selected pH (see Section 5.5).

B. Areas of Application

Power plants and ambient air sampling.

C. Applicable Concentration Range

From 0.01 ppm (ambient sampling) to 2000 ppm (using 1-3% H_2O_2) for source sampling.

D. Precision and Accuracy

Varies with analytical method (see sampling statistics).

E. Interferences

Interferences depend on the determination step. If a method specific for sulfate is used, the only interferences are oxidizable sulfur compounds. Where a non-specific method is used, e.g., titration with standard base, strong acid or basic species may interfere.

F. Comments

The main reasons for wide acceptance are high collection efficiency (514,515), ease of interfacing the scrubbing solution with analytical methods, good reproducibility of results, and negligible interference from weakly acidic species such as CO_2 or organic acids.

G. Conclusions

This procedure has a wide range of application; interferences are minor. Total sulfur oxides can be determined easily by collecting SO_2 and SO_3 in the peroxide solution or, if desired, SO_2 can be collected alone after removal of SO_3 .

5.4.2.2 Sodium Hydroxide

A. Description of the Method

The LA APCD (1) collects SO_2 in sodium hydroxide after prior removal of SO_3 by the controlled condensation method. Most users (76,204,210,195,252) collect both SO_2 and SO_3 simultaneously in a bubbler containing sodium hydroxide. In the latter method, an inhibitor must be added to prevent oxidation of

sulfite ion to sulfate. Berk and Burdick (210) employ benzyl alcohol, para-amino phenol hydrochloride and mannitol as inhibitors. Wickert (252) uses formaldehyde and Haller (384) and others (195,312) add glycerol to prevent oxidation of sulfite.

B. Areas of Application

Power plants.

C. Applicable Concentration Range

Wide.

D. Precision and Accuracy

Will depend on the analytical method selected, but generally poor. Preliminary analysis of field samples indicates that the precision may be as poor as $\pm 7\%$ for duplicate samples.

E. Interferences

One must correct for the amount of CO_2 absorbed in the caustic solution in order to obtain the total volume of gas sampled. In the Berk and Burdick procedure, CO_2 presents a problem in the analytical method. This is corrected for by titration to pH 4.1. However, organic acids have been found to interfere with the Berk and Burdick procedure (76). Caustic solution is a good scrubber for acidic components in the flue gas, e.g., NO_2 , N_2O_3 and HCl (for coal fired units) which interfere with many analytical methods.

F. Comments

Berk and Burdick (210) and API (204) titrate an aliquot of the caustic solution with acid to obtain total SO_2 and SO_3 . Benzidine chloride is added to a separate aliquot to determine SO_3 by the benzidine sulfate method. Smith (76) oxidizes

the caustic solution with peroxide and determines total SO_2 and SO_3 by the benzidine sulfate method. He also describes a "modified" Shell method (76) which follows collection in caustic solution, by oxidation with H_2O_2 and titration with barium ion using thorin indicator. Wickert (252) and LA APCD (1) oxidize the sulfite to sulfate to determine sulfate gravimetrically by precipitation with BaCl_2 . Atkin (195) determines SO_2 as sulfite by reaction with fuchsin and formaldehyde (the precursor of the West-Gaeke procedure). Axford and Sugden (312) determine sulfite polarographically.

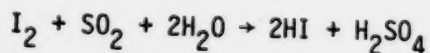
G. Conclusions

This approach is subject to a wide variety of interferences and errors in the collection and analysis of samples. (See Section on sampling statistics.) Oxidation of sulfite is a problem (as may be seen from the variety of inhibitors used) which is still not solved.

5.4.2.3 Iodine

A. Description of Method

The gas is bubbled through a standardized starch-iodine solution until the solution is just decolorized.¹ The gas volume needed for decolorization is measured by flowmeter or integrating meter. A modification of the standard procedure increases the KI concentration from 25 to 125 g/l to reduce the I_2 vapor pressure (410). This is claimed to prevent I_2 loss and increase method precision. The reaction with SO_2 is:



B. Areas of Application

This method is widely used in sulfuric acid plants (Reich Test) (95,192), power plants (170,215,504,379) and paper mills (410).

C. Applicable Concentration Range

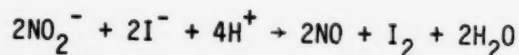
Has been used over a range of 200-2000 ppm (379).

D. Precision and Accuracy

Accuracy and precision of the Reich test are influenced by gas pressure, gas temperature, gas flow rate, and accuracy of volume measurement. BSI (379) reports a precision of $\pm 1\%$ at 2000 ppm but at 200 ppm precision falls off to $\pm 5\%$. The accuracy may be seriously affected by interferences in the flue gas. (See Section 6.2.)

E. Interferences

Any compound which reacts with iodine or iodide will interfere. This includes aldehydes, unsaturates and many other organic compounds as well as H_2S and mercaptans. Oxidants such as ozone, nitrogen oxides, and to some extent oxygen will reoxidize iodide to iodine and lead to false results. The oxides of nitrogen are a major problem since nitrate reacts with iodide ion in acid solution as follows (545):



F. Comments

The advantages of iodine absorption are speed and ease of determination (SO_2 concentration can be directly measured as a function of volume through-put). The disadvantages are sensitivity to light, non-specificity due to reaction of iodine with other compounds in the sample, some degree of endpoint uncertainty, iodine volatility and the need to use freshly standardized solutions.

G. Conclusions

This method works best in a well defined system, free of NO_x interferences such as a sulfuric acid plant. It can be used where a fast approximation of SO_2 content is desired, the SO_2 level is fairly high, and the operators are aware of the limitations. We do not recommend its use as an accurate method in a power plant because of the reaction with the oxides of nitrogen.

5.4.2.4 Sodium Tetrachloromercurate

A. Description of Method

Hendrickson et al (13), in a manual for the sampling and analysis of kraft mill recovery gases, recommend sampling stack effluent for SO_2 by trapping with a sodium tetrachloromercurate solution. Determination is done by the West-Gaeke method. (140)

Graue, Gradtke, and Nagel (128) in Germany collect SO_2 by taking a grab sample of the stack gas in a container of precisely known volume and diluting the sample down to ambient level with clear air. The diluted sample is collected in a bubbler containing sodium tetrachloromercurate solution. Sample analysis is done by the West-Gaeke method.

Borgwardt, Shigehara and Hartlage (499) collect a small volume of stack gas using a displacement technique. The sampling apparatus is heated to prevent condensation. They then transfer the gas sample to a syringe containing 20 cc of tetrachloromercurate solution. The SO_2 is determined by the West-Gaeke procedure. Borgwardt et al compare the West-Gaeke results to both the Shell* method and gravimetric method (absorption in NaOH). The W.G.

*Collection in peroxide and titration with Barium Chloride using Thorin indicator.

results are 8-14% lower than the Shell method and 4-8% lower than the gravimetric method for different sets of runs. These low values may be explained by side reactions occurring when stack gas is absorbed directly in the tetrachloromercurate solution (128).

B. Areas of Application

Kraft mill recovery gases (13), flue gas (128).

C. Applicable Concentrations Range

Can be applied to any sample concentration if diluted to a final SO_2 concentration less than 5 ppm.

D. Precision and Accuracy

Unknown.

E. Interferences

Any species that reacts with mercuric ion is a potential interference. (Metals, sulfides, etc.) NO_2 bleaches the West-Gaeke color.

F. Comments

Side reactions have been reported to occur with undiluted gas in the scrubbing solution (128,265). Therefore, the effluent must be diluted. (No detailed explanation given.) As a result of the required sample dilution, minor components such as SO_3 , have to be measured separately. The necessity for grab sampling rules out the advantages inherent in continuous sampling. In addition, the dilution process is complicated and time consuming.

The sodium tetrachloromercurate approach, which is specific for SO_2 , has always been combined with the West-Gaeke method for SO_2 measurement, requiring low concentrations of SO_2 in the

final sample to be analyzed. It is not clear at this time, whether modification can be made to permit collection of SO_2 at high concentration levels directly from flue gas samples.

G. Conclusion

On the basis of present work this method is not attractive. However, since it is one of the few methods which is specific for SO_2 , it should be closely examined.

5.4.2.5 Stannous Chloride (385)

A. Description of Method

The sample is collected in a bubbler containing $\text{SnCl}_2\text{-HCl}$ solution which reduces SO_2 to H_2S . The H_2S formed reacts with a solution of ammonium molybdate to give a solution of molybdenum blue, which is measured colorimetrically.

B. Areas of Application

Stratmann (385) describes a method for the determination of SO_2 in the presence of H_2S in both flue gas and ambient air samples, where the amount of H_2S is small relative to the SO_2 concentration. A means to eliminate any H_2S in the sample by bubbling the entire sample through a solution of ammonium molybdate is suggested. SO_2 is said not to react with this solution.

C. Applicable Concentration Range

Has been used for ambient and stack concentrations.

D. Precision and Accuracy

Reported precision is better than $\pm 10\%$ (duplicate analysis) for ambient sampling and better than $\pm 2\%$ (duplicate analysis) for stack sampling.

E. Interferences

H_2S oxidants, and metallic ions. The latter will complex with the H_2S formed; oxidants, including oxygen, will destroy the effectiveness of the stannous chloride.

F. Comments

Many potential sources of trouble and needs fine control before use.

G. Conclusions

This appears to be a difficult procedure to apply to stack gas samples because of the instability of stannous chloride solutions.

5.4.2.6 Sodium Acetate (116)

A. Description of Method

SO_2 has been separated from H_2S and other sulfides found in kraft pulp mill effluent by selective absorption of the SO_2 in 0.2 N $\text{NaC}_2\text{H}_3\text{O}_2$. The method is based on the relative acid strengths of sulfurous acid > acetic acid >> H_2S . Thus, SO_2 will be absorbed by the acetate solution while H_2S will not.

B. Areas of Application

Kraft pulp mill effluent.

C. Applicable Concentration Range

Absorption is said to be quantitative at SO_2 concentrations up to 1.5 g/M^3 .

D. Precision and Accuracy

Total method error reported to be 5-10%.

E. Interferences

Acid and basic gases (and other sources depending on the analytical procedure selected).

F. Comments

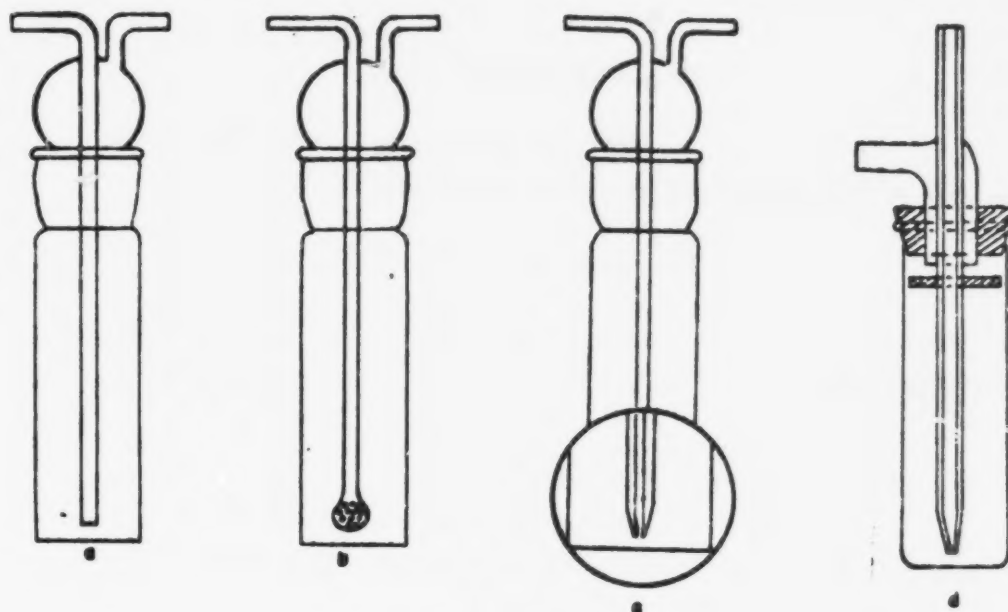
The method requires close control of pH, thus the presence of acidic or basic gases is a serious problem.

G. Conclusions

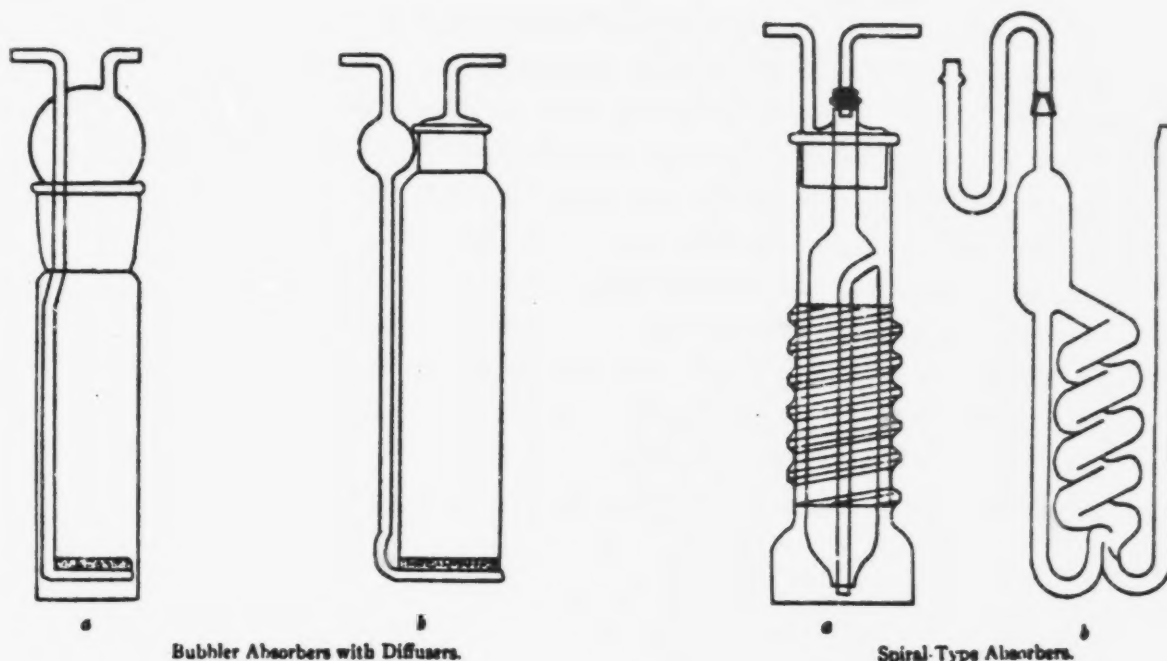
This method does not offer any advantages over hydrogen peroxide collection for collection of a sample from a fossil-fuel effluent.

5.4.2.7 Collection Efficiency of Aqueous Scrubbers

Little information is available on the collection efficiency for the various absorbing solutions used for kraft mill effluents. However, there are data on the collection efficiencies of the major scrubbing solutions commonly used for fossil fuel combustion (H_2O_2 , I_2 , and NaOH). For caustic and iodine collection systems, bubblers are commonly used. With peroxide, where collection efficiency is considerably higher, the design of the device is not as critical and a variety of absorbers such as illustrated in Figure 5-8 have been used. Comparative efficiencies of selected devices for the several major scrubbing media are given in Table 5-9. It is seen that quantitative collection (99%) is readily obtained in all instances employing two series scrubbers.



Simple Bubbler Absorbers.



Bubbler Absorbers with Diffusers.

Spiral-Type Absorbers.

Figure 5-8. Scrubber Configurations (542)

TABLE 5-9
EFFICIENCIES OF ABSORBING DEVICES AND REAGENTS FOR SO₂

Device	Flow Rate	Absorbing Reagent	Eff. %	Ref.
Large Impinger	1 cfm	NaOH	80-90	503
		H ₂ O ₂	90-100	515
		I ₂	90	503
Fritted Bubbler	5 l/m	NaOH	95	503
		H ₂ O ₂	95+	
Multijet Bubbler	10-15 l/m	H ₂ O ₂	98-100	515
Midget Impinger	.5 l/m	H ₂ O ₂	90-95	516

In order to determine flow rate dependence, SO_2 collection efficiencies were measured for two midget impingers in series each containing 15 ml of freshly prepared 1% hydrogen peroxide solution. The dilution system used is given in Appendix 5. Total sample volumes ranged from 15 to 30 liters. Sulfate analyses were performed by the barium chloranilate method.

For high efficiency scrubbers, the collection efficiency may be determined by analysis of both impingers to obtain the fraction collected in the first, independent of source description. For a given collection medium, the collection efficiency is assumed to be a function of SO_2 concentration, total flow rate, temperature and device geometry (pressure, except as influenced by flow pressure drop, constant).

As a preliminary experiment to determine reproducibility in the system and to investigate possible variability between impingers, five consecutive runs were conducted at constant flow rate, temperature and SO_2 concentration with five different midget impingers of identical design.* The results (Table 5-10) show that the collection efficiency is not a strong function of impinger parameters. The standard deviation of the collection efficiency determined experimentally ($\pm 2\%$) is roughly in the range expected from the precision of the analytical and sampling methods combined. Any variation between impingers, for this limited population, is, therefore, small.

The collection efficiency has been determined as a function of flow rate at two concentration levels. The observed collection efficiencies (calculated from the fraction collected in the first of two series impingers) are given in Table 5-11 and plotted in Figure 5-9 as a function of flow rate. At 875 ppm, the decrease in collection efficiency with increasing flow rate, although apparent, is sufficiently gradual so that essentially quantitative (99%) collection efficiency is maintained to flow rates of 5 liter/min for two impingers in series. At the higher concentration, 1740 ppm, collection efficiency drops more rapidly (at rates above 1.5 liter/min) so that the 99% collection efficiency limit for two series impingers occurs at about

*Ace Glass, Inc., Cat. No. 7531.

TABLE 5-10
COLLECTION EFFICIENCIES OF SINGLE MIDGET IMPINGERS FOR SO₂^a

Impinger	Collection Efficiency (%) ^b
1	94
2	99
3	94
4	97
5	<u>97</u>
mean ± standard deviation	96 ± 2.2

a $t = 22 \pm 1^\circ\text{C}$; flow rate 0.5 liter/min; SO₂ concentration
~ 875 ppm in air; 15 ml 1% H₂O₂

b determined by amount found in second midget impinger

TABLE 5-11
COLLECTION EFFICIENCY OF MIDGET IMPINGERS FOR
SO₂ IN PEROXIDE^a

Replicates	SO ₂ , ppm	Flow Rate (liter/min)	1st impinger ppm SO ₂	2nd impinger ppm SO ₂	Total SO ₂ , ppm	Collection Efficiency 100 × #1/(#1 + #2)
5		0.5	853	37	890	96
3		1.5	831	40	871	95
3	875	3.0	794	65	859	92
3		5.0	774	80	854	91
3		1.5	1640	70	1710	96
2	1740	3.0	1525	150	1675	90
3		5.0	1420	230	1650	86

^a T = 22°C; 15 ml 1% H₂O₂

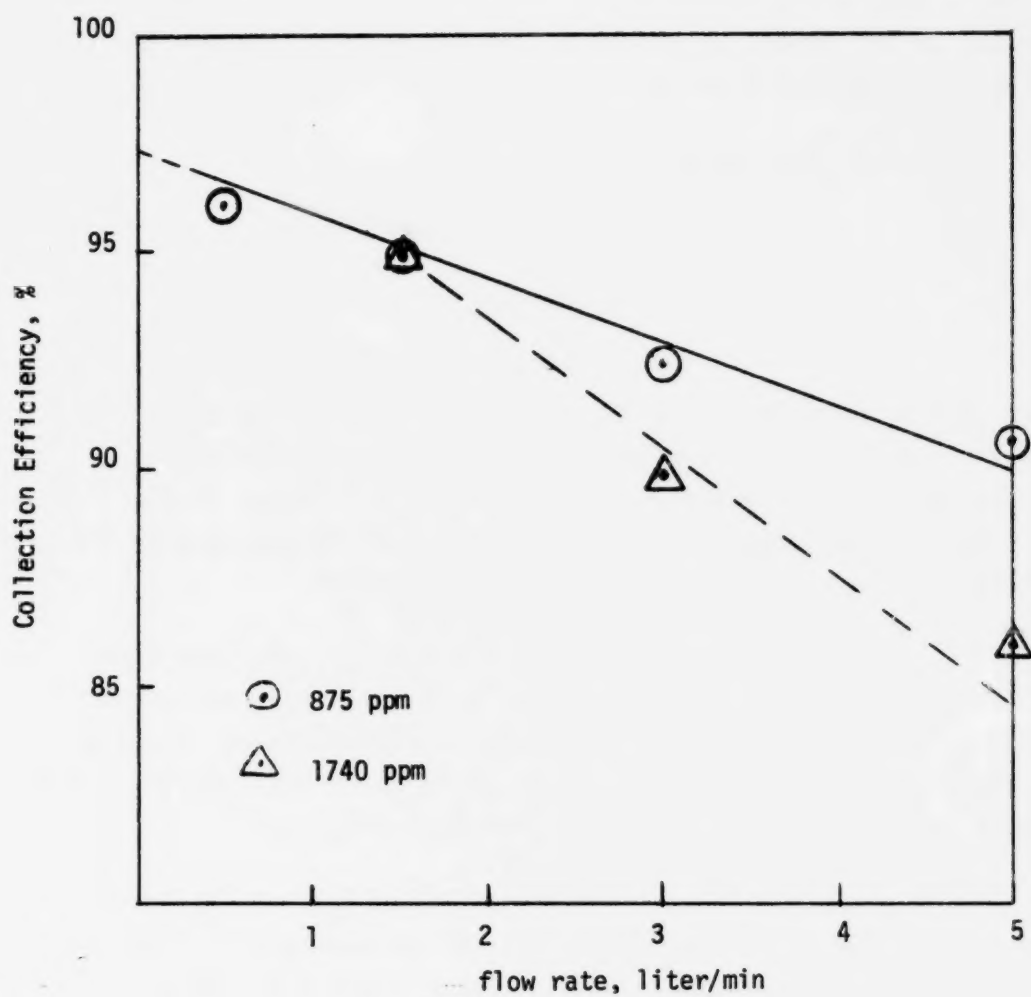


Figure 5-9. Collection Efficiency of a Single Midget Impinger for SO_2

3 liter/min. Blowover of peroxide solution was observed at flow rates $\geq$ 3 liter/min, leading to possible loss of sample.

The collection efficiencies of single impingers were also determined at 39°C and found to be somewhat better at the higher temperature (~98% for both 875 and 1740 ppm SO₂).

It is concluded that the collection efficiency is not a very strong function of either sample flow rate or SO₂ concentration in the regions of interest. The recommended flow rate for quantitative collection in two series impingers is 0.5-3.0 liter/min.

5.4.3 Solid Adsorbents

5.4.3.1 Silica Gel

A. Description of the Method

a) Untreated Silica Gel - Silica gel has been used as an adsorbent for SO₂ both in ambient air and in paper mill stack effluents. This technique is used in Swedish paper mills (154) as a rapid quantitative determination for SO₂ up to 100 ppm. A sample is adsorbed at room temperature and desorbed at 120-150°C by heating the gel. Detection is by gas chromatography.

b) Treated Silica Gel - Patterson and Mellon (182) and Kitagawa and Kobayashi (376) have developed treated gels such as ammonium vanadate-gel, iodate or periodate-gel and have investigated other inorganic and organic-gel formulations. Kanno (125) has tested Kitagawa detector tubes in power plant effluents.

A separation of H₂S and SO₂ has also been effected by using a silica gel column impregnated with silver sulfate and potassium hydrogen phosphate (396). Ammonia is the only serious interference - the gel must be acidic or SO₂ is retained as well as the H₂S. SO₂ is determined by H₂O₂ oxidation followed by Thorin titration. However, this approach needs more careful study before being recommended for widespread usage.

Stratmann (137) developed a method for SO_2 by adsorption on silica gel followed by reduction to H_2S at 700-900°C over a platinum catalyst. The H_2S was then determined by the molybdenum blue method.

B. Areas of Application

Ambient air (376), paper mills (154), stack effluents.

C. Applicable Concentration Range

Can be applied to total range of interest.

D. Precision and Accuracy

Using the silica gel-silver sulfate approach (396), precision is reported to be about $\pm 10\%$ and accuracy is indicated to be 85-95% for amounts of SO_2 from 1-11 mg in the presence of up to 1200 μg H_2S .

No data are given on untreated silica collection (154).

As a result of the surprisingly good determinations obtained by Kanno in stack effluents ($\text{CV} \approx 5\%$, see Section 6.4), we have compared the Kitagawa detector tube to peroxide collection for a laboratory SO_2 -air mixture. The results obtained are given in Table 5-12 and plotted in Figure 5-10.

The measurements were made at three SO_2 levels with and without the moisture tubes recommended for flue gas analysis. Under the conditions tested and within the limitations imposed by the restricted range of the experiments, we conclude:

1) Without moisture tubes, the SO_2 detector (Kitagawa) tubes give higher readings than actual.

TABLE 5-12
COMPARISON OF DETECTOR TUBE^a TO PEROXIDE
IMPINGER COLLECTION FOR SO₂^b

Actual ^c ppm SO ₂	Moisture Tube	ppm SO ₂ Measured with Detector Tube
660	No	800
660	Yes	600
1680	No	1900
1680	No	2100
1680	Yes	1100
2170	Yes	1400
2170	Yes	1600
2170	No	2500

a Unico Environmental Instruments, Inc., Fall River, Massachusetts,
Cat. No. 103 bf, Kitagawa Detector Tubes for Sulfur Dioxide in Flue
Gas (0.02-0.30%)

b These measurements were made with synthetic, dry samples at room
temperature. For sampling of flue gases, the manufacturer recom-
mends a probe temperature greater than 120°C, although the detector
tubes are not heated. Calibration is stated to be unaffected for
detector tube temperatures in the range 0-40°C.

c As determined by titration of peroxide impinger.

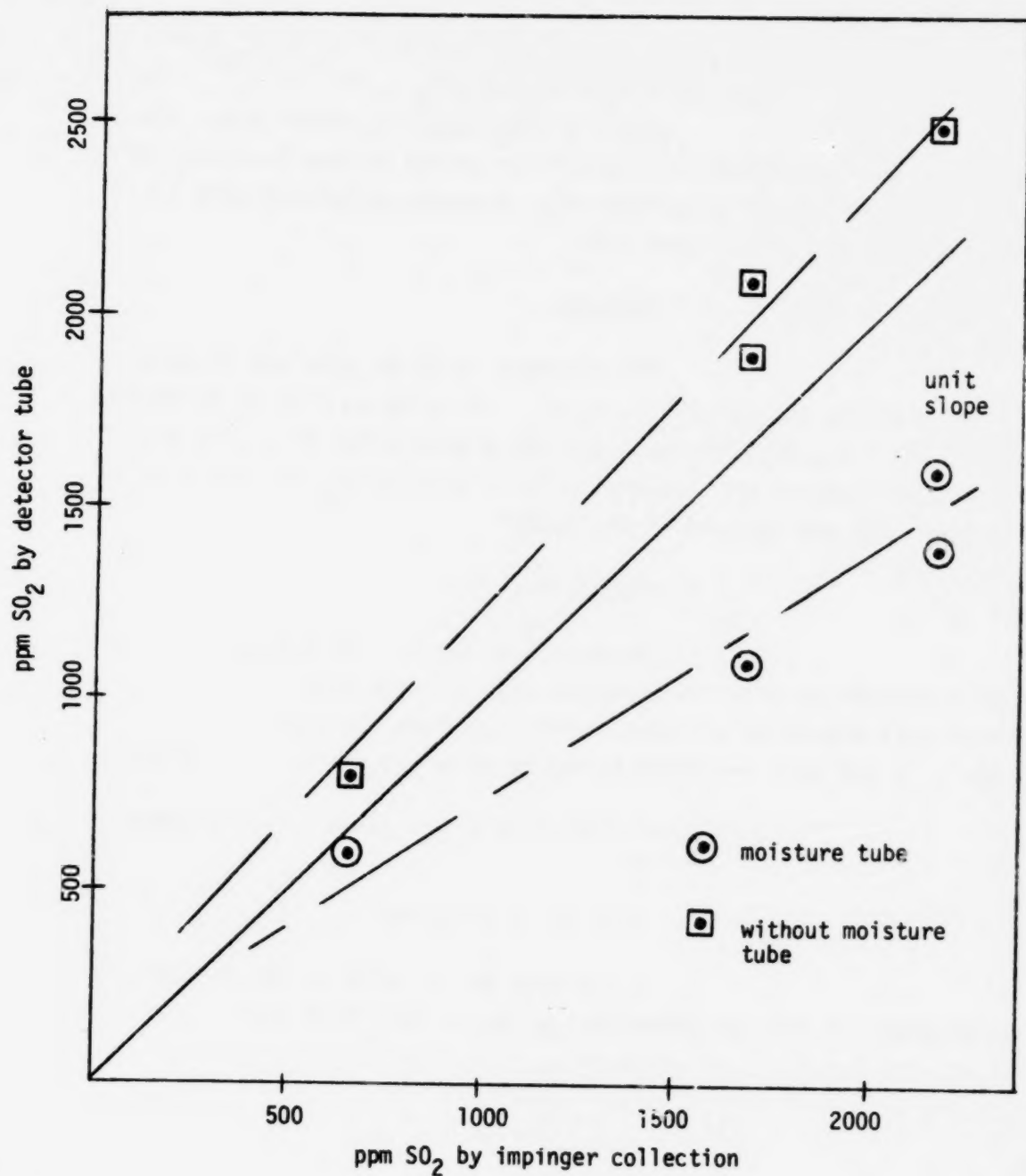


Figure 5-10. Comparison of Detector Tube and Peroxide Collection Analysis for SO_2

2) With moisture tubes, the apparent SO_2 concentration is lower than actual.

3) Although the precision and accuracy of the detector tube is not nearly as good as Kanno reports, the technique is attractive because of its simplicity.

E. Interferences

Depends on impregnating agents used. However, none are totally specific for sulfur oxides so that there will be potential interferences including: H_2S , unsaturated hydrocarbons, carbon monoxide, aldehydes, water, etc.

F. Comments

There appears to be no advantage in using untreated silica gel for collecting SO_2 . The advantages of using treated silica gel, i.e., detector tubes for the determination of SO_2 are the rapid color response obtained indicative of a given SO_2 concentration and the simplicity and rapidity of the method.

G. Conclusions

These methods would be of some utility where H_2S is present but offer no advantage over peroxide method for use in fossil fuel combustion effluents. Detector tubes, because of their simplicity and immediate readout, may be of use as a simplified method.

5.4.3.2 Adsorption on Molecular Sieve or Ion-Exchange Resins

A. Description of Method

Sulfur dioxide is collected on the semi-dry solid substrate and then determined by one of many techniques.

B. Areas of Application

Unknown

C. Applicable Concentration Range

Unknown

D. Precision and Accuracy

Unknown

E. Interferences

Unknown

F. Comments

Papers by Krejcar (231) in Czechoslovakia, and Cole and Shulman (139) and Layton and Youngquist (393) report on the sorptive characteristics of SO_2 on ion exchange resins. Data indicate SO_2 is quantitatively adsorbed up to the breakthrough point by both weakly and strongly basic resins. The breakthrough point depends upon the concentration of SO_2 and the linear velocity of gas. Gas phase adsorption on fresh resin is essentially irreversible until a monolayer cover has been added. Reversible sorption in the gas phase is possible using saturated resin (adsorption and desorption isotherms are identical), but the process is highly diffusion-limited. Bienstock and Field (185) at the Bureau of Mines have also worked on SO_2 adsorption and absorption. Their findings indicated molecular sieve 13x gives an adsorption of 7 grams of SO_2 per 100 grams of adsorbent which compares quite favorably with adsorption by activated carbon (8 grams SO_2 /100 grams adsorbent). Removal by desorption of SO_2 is not considered in this paper.

The emphasis to date has been to use ion-exchange or molecular sieve as a tool to remove SO_2 from gas streams. Therefore, there is not any information on this approach as a technique for measurement of sulfur oxides.

G. Conclusion

Ion-exchange resins appear to offer an interesting alternative for collection of SO_2 . This is especially true if

SO₂ and SO₃ can be collected together and then removed by aqueous elution techniques; however, this cannot be considered as a method at this time.

5.4.3.3 Reactive Solid Sorbents

In this section, we briefly discuss the potential applicability of reactive solid sorbents to the collection and subsequent determination of SO₂.^{*} An example of a reactive sorbent is the lead dioxide candle, which has been widely used as a passive (integrating) ambient sulfation rate monitor (96). Very recently, NAPCA-PCE has supported major programs to evaluate metal oxides (493,492) and other inorganic compounds (491) as possible sorbents for application to new processes for removal of SO₂ from flue gases. It is quite feasible on the basis of that work to select promising sorbents from the somewhat different point of view of analytical collection. Readout (following collection) will require analysis specific for sulfate, as in the lead dioxide candle technique.

A. Carbonates and Hydroxides

From the analytical point of view, FMC's (491) reaction classes may be reduced to the following (on the basis of maximum free energy of reaction) (Table 5-13).

The minimum value of K_p, K_p (min.), has been recalculated for an equilibrium effluent concentration of 1 ppm SO₂ for an effluent gas composition, which is satisfactory for analysis for SO₂ concentrations down to the order to 50 ppm. Utilizing these criteria, and noting that one is considering isolated reactions rather than competing multiple equilibria, we note the following potential sorbents at 400°K. The temperature (~250°F) has been selected for operation internal to the duct providing major advantages of representative sampling and

^{*}We have previously discussed reversible adsorbents and detector tubes (Sections 5.4.3.1 and 5.4.3.2). The latter are reactive indicating sorbents on an inert support

TABLE 5-13
STANDARD METAL COMPOUND REACTION CLASSES

Class No.	Reaction	Reaction	Kp	Kp (min.) $\times 10^{-4}$
I	M CO ₃ + SO ₂	$\pm$ M SO ₃ + CO ₂	P _{CO₂} /P _{SO₂}	14
II	M (OH) ₂ + SO ₂	$\pm$ M SO ₃ + H ₂ O	P _{H₂O} /P _{SO₂}	7
IV	M CO ₃ + 1/2 O ₂ + SO ₂	$\pm$ M SO ₄ + CO ₂	P _{CO₂} /P _{SO₂} · P _{O₂} ^{1/2}	81
V	M (OH) ₂ + 1/2 O ₂ + SO ₂	$\pm$ M SO ₄ + H ₂ O	P _{H₂O} /P _{SO₂} · P _{O₂} ^{1/2}	40

increased reaction rates. For all the reactions selected, K_p (min.) is in the range 10^5 - 10^6 for the conditions stated.

The data of Table 5-14 show quite clearly that carbonates of the strongly basic oxides (Class I) are thermodynamically feasible as sorbents and should be evaluated for analytical application particularly as hydrates stable in an effluent environment. Only the classical "strong bases" are theoretically suitable as SO_2 sorbents and are, of course, not applicable as such in an atmosphere containing CO_2 at an appreciable partial pressure (Class II). Class IV reactions are all favorable, reflecting the relative acid strength of SO_3 vs CO_2 , but are not of real interest since they require a catalytic high temperature oxidizer section to obtain appreciable reaction rates. Class V reactions have the same drawback.

It is of interest to note that alkali carbonate impregnated filter paper has recently been investigated as a passive sampler for ambient SO_2 and NO_2 (490,489).

B. Oxides

Thomas et al (493) conducted extensive thermodynamic analysis (and some kinetic studies) of metal oxides as potential (reversible) sorbents for SO_2 . From the different perspective of collection for analysis, one can again isolate a large number of potential solid absorbents which provide the desired low equilibrium vapor pressures of SO_2 . Two categories of oxides, oxidants and non-oxidants, may be used as sorbents for the oxides of sulfur. The first group includes PbO_2 , MnO_2 , CeO_2 , and possibly CrO_3 , although the latter is hygroscopic. PbO_2 has been used extensively for ambient sulfur oxide analysis. Although the candle method of analysis works very well, the formation of $PbSO_4$ is slow. MnO_2 and CeO_2 appear to be the most promising oxidizing sorbents. Procedures for producing the sorbent must be standardized to obtain reproducible activity, since the reaction rate depends upon the method of preparation (493).

TABLE 5-14
POTENTIAL SO₂ "ANALYTICAL" SORBENTS AT 400°K

Reactant(s)	CO ₃ ⁼	OH ⁻	CO ₃ ⁼ +O ₂	OH ⁻ +O ₂
Class (FMC)	I	II	IV	V
Log ₁₀ K (min)	5.147	4.835	5.908	5.603
Element				
Ba	+	+	+	+
Ca	-	+	+	+
Co	?	0	+	0
Cu (II)	-	0	+	0
Cu (I)	-	0	+	0
Fe (II)	-	0	+	0
Fe (III)	-	0	+	0
Li	+	+	+	+
Mg	-	-	+	+
Mn (II)	-	-	+	-
Mn (III)	-	0	+	0
K	+	0	+	0
Na	+	+	+	+
Sn (IV)	-	0	+	0
Zn	-	0	+	0

+ thermodynamically favorable

- thermodynamically unfavorable

? approximately equal to K_p

0 no information in ref. (491)

The oxides, which simply react with SO_2 and SO_3 to form sulfites and sulfates respectively, appear less promising. Oxides have to be chosen, which are stable in an effluent atmosphere and which do not form carbonates preferentially. BaO , ZrO_2 , CdO , PbO , Bi_2O_3 , and Ce_2O_3 appear to be possibilities (493). Appreciable sulfite formation may not occur except at elevated temperatures, requiring an auxiliary furnace. Absorption begins at a relatively low temperature on Cr_2O_3 and SnO_2 (mixed) but even then it is slow below 300°C . The oxides listed above were not experimentally investigated as sorbents because of the high decomposition temperatures of their sulfites and sulfates or because of disproportionation of the sulfite, and their usefulness is therefore unknown. However, BaO forms a sulfite between 30 and 800°C , and may well be a good oxide sorbent.

A number of mixed oxides have also been investigated (492) in which an active sorbent is precipitated on an inert support, exposing a large sorbent area to the sorbate. The best of these, investigated by AVCO are CuO supported on alumina or silica and manganese oxide, supported on alumina. For these materials, adsorption is fast. Mn-Al-2 , for example, at 300°C adsorbs at an initial rate of $400 \text{ gms } \text{SO}_2/100 \text{ gm sorbent/hr/mole fraction of } \text{SO}_2$. (Mn-Al-2 is manganese oxide, supported on aluminum oxide, where Mn-Al-2 denotes the method of precipitation.) From the time of half absorption capacity exhaustion (13 min. at $0.3\% \text{ SO}_2$), it may be estimated that the Mn-Al-2 composition may be a suitable analytical sorbent for grab sampling; i.e., for short duration (approx. 1 min.) samples where the absorption rate remains high. It is important to note that these materials have been selected on the basis of engineering criteria for flue gas cleaning and have not been optimized for sampling.

As a result of the potential of solid sorbents for both simplified and high precision methods, we have briefly examined the behavior of PbO_2 as a sorbent for SO_2 .

C. Experimental Studies of the Collection Efficiency of SO_2

We have conducted a preliminary investigation of the collection efficiency for SO_2 by solid PbO_2 . The initial experiment, utilizing Research Appliance Corporation PbO_2 (for sulfation candles) was unsuccessful since an unacceptably large pressure drop developed across a 6-cm column. A coarser grade (Fisher Scientific, Special Micro Grade, 12-20 mesh) proved completely satisfactory.

The PbO_2 was loosely packed into 6 mm i.d. glass tubing and secured with glass wool plugs. The SO_2 -in-air test mixture was passed through the PbO_2 adsorber and then through an impinger containing peroxide to collect the remaining SO_2 . The calculated SO_2 concentrations obtained from the dilution system were checked before and after each days run by collection of SO_2 in two peroxide impingers in series.

The collection efficiency of the PbO_2 adsorber was determined from the known SO_2 concentration, the volume of gas sampled and the amount of SO_2 found in the series impinger. The results obtained are summarized in Table 5-15. At ambient temperature, quantitative collection is observed (within the precision of the experiment) for a 12-cm column at 875 ppm SO_2 and for a 15-cm column at 1740 ppm, both at a flow rate of 1.0 liter/min.

These results suggest a surprisingly high rate of SO_2 absorption, for this specific PbO_2 , and confirm the high potential of solid adsorbents for SO_2 collection.

Gully et al (616) have investigated solid sorbents for the purpose of removing acid gases from space cabin atmospheres. They utilized standard concentrations of about 10-20 ppm for various gases including SO_2 and determined the exit gas concentrations as a function of time. The collection efficiency may be calculated from the initial ratio of the inlet/outlet concentrations. They used heated ($\sim 300^\circ\text{C}$) columns 1-2 cm in length for their measurements and gas flow

TABLE 5-15
COLLECTION EFFICIENCY OF SOLID PbO_2 FOR SO_2 ^{a,b}

Run	SO_2 Concentration	Length of PbO_2 (cm)	Collection Efficiency (%) ^c
1	875	9	92
2	875	12	98
3	875	12	99
4	875	12	99
5	1740	15	98
6	1740	15	98

a Fisher Special Micro Grade, 12-20 mesh

b Sampling rate = 1 liter/min for 15 minutes at 23°C

c Determined from amount in series impinger

rates of ~300 ml/hour. The flow rates in our PbO_2 experiments were about 100 times greater as were the column lengths so that residence times are comparable in both cases. A summary of efficiencies for collection of SO_2 calculated from their results is given in Table 5-16. Even at ~350°C, the Li, Ca, and Ba carbonates do not provide quantitative collection of SO_2 . Sodium carbonate and bicarbonate provide useful collection efficiencies at the elevated temperature studied. Manganese dioxide appears quite promising since the collection efficiency is quantitative (99%). Gully indicates further that studies of MnO_2 at room temperature also show high efficiency but no data are provided to support this statement. It is clear from both our brief studies and the work of Gully et al that the oxidative solid sorbents are quite promising for collecting the sulfur oxides.

D. Conclusion

Although it is theoretically feasible to consider fixation of sulfite and sulfate and subsequent determination of

TABLE 5-16
COMPARISON OF COLLECTION EFFICIENCIES OF SOLID SORBENTS FOR SO₂^a

ppm SO ₂	Collection Efficiency (%) ^b	Sorbent
13-14	40	CaCO ₃
12	47	Li ₂ CO ₃
10	48	BaCO ₃
14	95	NaHCO ₃
15	91	Na ₂ CO ₃
15	99	MnO ₂

a T = 342°C, flow rate 300 ml/hr

$$b \text{ Collection efficiency} = \left(\frac{C_i - C_f}{C_i} \right) \times 100$$

where C_i and C_f are the inlet and outlet concentrations

each species, it is our present belief that the most promising immediate prospect for reactive adsorbents is for simple total SO_x determination (possibly +NO_x).

5.4.4 Dilution Methods

One may, in principal, dilute a stack effluent containing SO₂ and SO₃ down to ambient levels and use one of the analytical techniques described by Hocheiser (96). However, for a ten-fold, or more likely, a hundred-fold sample dilution, minor components such as SO₃ will be lost.

Several different dilution techniques may be employed. One dilution technique for SO₂ (described in Section 5.4.2.4), which involves taking a grab sample and diluting this with air, provides only the instantaneous pollutant concentration. The grab sampler has to be heated while

collecting and diluting the sample to prevent condensation of moisture and subsequent loss of the SO_2 .

Dilution techniques have been used frequently in automobile exhaust studies. One such technique is the variable dilution technique described by Rose et al (497). Another method which could be used involves two calibrated critical orifices. The stack gas is diluted with air, then collected in bubblers containing various absorbing solutions (96). Thus, the sample could be collected over a long enough period of time to obtain a good estimate of the average plant output. The dilution section should be heated to prevent condensation.

The major drawbacks to dilution methods used with manual methods of analysis are:

1. Loss of minor components in stack gases.
2. Collection efficiencies of various absorbing solutions usually decrease at lower concentrations.
3. "Clean" dilution air is required.
4. The apparatus is complex and cumbersome.
5. Interferences not commonly found for ambient methods may be a problem at stack concentrations (this situation may be very critical for coal-fired plants).
6. Precision and accuracy of the wet chemical methods usually decrease with concentration.

As a result of these problems, we do not recommend this technique.

5.5 Comparison of Analytical Methods

5.5.1 Introduction

All practical methods for determination of SO_3 depend upon analysis in an aqueous solvent. The resulting H_2SO_4 may be measured as sulfate or titrated as acid by the variety of techniques described below. For SO_2 collection, many methods include an oxidation

reaction either in the absorbing solution or subsequent to absorption and determination as sulfate.

However, SO_2 may also be determined as sulfite, although this method has not been widely used. (Another option for the analysis of SO_2 is reduction to H_2S with SnCl_2 and determination by the molybdenum blue technique.. See Section 5.4.2.5.) The alternatives are discussed in following sections.

5.5.2 Analytical Methods for the Determination of Sulfate Ion or Sulfuric Acid

5.5.2.1 Titration with Barium Ion and Selected Indicators (52,78,145,169,303,308,345,353,129,196,193. Also see Section 5.5.4.1)

A. Description of Method

A solution containing sulfate ions is titrated with a standard barium chloride or barium perchlorate solution using an adsorption indicator (such as thorin). The titrant is preferably $\text{Ba}(\text{ClO}_4)_2$ due to its greater solubility in alcoholic solution. The problem of coprecipitation is diminished by using the perchlorate instead of the chloride anion (196).

B. Areas of Application

Fritz and Yamamura (303) developed this method for the analysis of boiler water and raw and treated city water. The technique has been extended to stack gas sampling by Seidman at Shell Development Co. (78), Fielder and Morgan (169) and others (52,145,300). A microchemical method for sulfur oxides in ambient air (308) also uses barium ion titration.

C. Applicable Concentrations

Thorin	down to 10 ppm, upper limit unknown
Tetrahydroxy quinone	10 ppm up to 30,000 ppm
Alizarin Red S	no range given

D. Precision and Accuracy

Thorin	$\pm 0.4\%$ at 25 $\mu\text{g SO}_3/\text{ml}$
	$\pm 4\%$ at 2.5 $\mu\text{g SO}_3/\text{ml}$
Tetrahydroxy quinone	$\pm 2.4\%$
Alizarin Red S	about 1% indicated

E. Interferences

All barium sulfate precipitates are subject to both cation and anion interferences due to coprecipitation. Cation removal is necessary for all three indicators since colored complexes are formed with the indicators which mask the endpoint of the titration. Sulfite and phosphate are reported to cause serious interference with the thorin titration (303). Phosphate interference with thorin is removed by precipitation with MgCO_3 . Phosphate interference with tetrahydroxy quinone is removed by pH adjustment.

F. Comments

Alizarin Red S and tetrahydroxy quinone are reported to give poor endpoint definition and are not usable to as low a concentration as thorin (303). In addition, thorin has been found to be more precise than Alizarin Red S (196).

G. Conclusion

Thorin appears to be the best of the three indicators compared.

5.5.2.2 Titration with Barium Ion Using Other Substituted Naphthalene Disulfonic Acid Derivatives (SNDAD) as Indicators (60,392,394,395,430,405)

A. Description of Method

Alcohol or acetone solutions of sulfate ions are titrated using SNDAD. The titrant is usually $\text{Ba}(\text{ClO}_4)_2$ but with arsenazo III (2,7-bis (azo-2)-phenyl arsono-1,8-dihydroxynaphthalene-3,6-

disulfonic acid disodium salt) a mixture of barium and lead acetate is employed (617,430).

B. Areas of Application

Any solution containing sulfate ions. Bredesinsky (392,394,395,405) has used SNDAD's to determine the sulfur content of both organic and inorganic compounds after conversion to sulfate. Kanno (125) and Fukui (60) have used the arsenazo III method for SO_2 analysis in stack gases.

C. Applicable Concentration Range

Range is claimed to be greater than for thorin (60) but no lower limit is given.

D. Precision and Accuracy

Not given for arsenazo III. Other SNDAD indicators, $\sigma = \pm 0.08 - 0.14\%$ (394).

E. Interferences

No interference is claimed from H_2O_2 , Cl^- , NO_2^- , or NO_3^- . No interference was found from sulfite ion added in 300-fold excess of the sulfate ion concentration. Solution has to be kept below pH 3 (60).

F. Comments

Titrations with arsenazo III or other SNDAD's are claimed to be superior to thorin. Lack of interferences and greater ease of endpoint detection are two good reasons for the superiority claim (60).

G. Conclusion

Arsenazo III (or related) indicator appears to be very useful for a titration procedure (provided the endpoint is actually as easy to see as stated, but see Section 5.5.4.1A).

5.5.2.3 Titration with NaOH (35,55,80,81,127,180,403)

A. Description of Method

A solution containing sulfuric acid formed by the oxidation with H_2O_2 is titrated with standard sodium hydroxide to a selected endpoint. Bromphenol blue (35,55,80,81,127) and methyl red (180) have been used as indicators. The amount of titrant used determines the solution acidity and thus the sulfate ion concentration, provided no additional acidic species are present.

B. Areas of Application

This method has been used in both chemical plants (180) and power plants (35,55,80,81,127,403,430).

C. Applicable Concentration Range

Wide. Lower limit unknown. JIS K103 (430) does not recommend use of this method below 500 ppm SO_2 because of the problem of interferences from acidic components in flue gases.

D. Precision and Accuracy

Precision - 1% or less; accuracy - depends on interferences present.

E. Interferences

This is an acid-base titration; NH_3 , oxides of nitrogen, and other basic or acidic species in the gas sample will influence the volume of titrant needed to produce a color change.

F. Comments

Since this is an acid-base reaction, it is not a specific method, and thus is not desirable for use where high accuracy is desired.

G. Conclusion

Due to non-specificity, this method is not as desirable as titration with barium ion.

5.5.2.4 Colorimetry Using Barium Chloranilate (153,159, 164,271,273,311,361,424,425,430. Also see Section 5.5.4.2 and Appendix 3.)

A. Description of Method*

Barium chloranilate is added to a buffered alcoholic solution containing sulfate ions. The sulfate ions react with the barium chloranilate to yield barium sulfate and the acid chloranilate ion. The amount of acid chloranilate liberated is proportional to the sulfate ion concentration. Buffering is required because the solution absorbance is a function of pH. The reaction is run in 50-80% alcohol to decrease the solubilities of barium sulfate and barium chloranilate.

B. Areas of Application (153,164,271,273,311, 360,424,425)

This method is being used for flue gas sampling, ambient air sampling (159), and as a means of determining traces of sulfur in naphthas by lamp combustion (361). At least two instruments have been constructed using the barium chloranilate method for SO_3 in power plants (153,437).

C. Applicable Concentration Range

The method is claimed to be applicable from 2-400 ppm sulfate (164). Determination at 330 nm rather than 530 nm is reported to allow detection down to 0.06 ppm (311).

D. Precision and Accuracy

Precision of 1-3% and 99% accuracy has been reported for determinations made at 530 nm (164,273).

*See Appendix 3 for full description.

Precision of 5-20% is reported for the 330 nm determination (311).

E. Interferences

Cation contamination must be either prevented by a particulate filter in the sampling line or removed by an ion exchange resin, before reaction with the barium chloranilate. Interference from cations is due to colored species formed with the chloranilate ion which decrease the available amount of chloranilate in the mixture and may also interfere with the absorbance measurement. Common anions such as nitrate and chloride are said not to interfere (164). The presence of 0.15% H_2O_2 has been reported to give no interference (424).

F. Comments

The method is simple to perform, has several pH options, and two wavelength readouts, depending on the needs of the analyst. Instrumental readout aids in minimizing operator error.

G. Conclusion

The analysis is easily performed, even with unskilled operators. This appears to be one of the best available methods for sulfate analysis.

5.5.2.5 Turbidimetry (160,165,170,215,218,221)

A. Description of Method

Excess barium chloride solution is added to a solution containing sulfate ions and the resulting turbidity determined.

B. Areas of Application

Used in England by several power companies for the determination of SO_2 and SO_3 in flue gas (see references above).

C. Applicable Concentration Range

Unknown.

D. Precision and Accuracy

±2.7% at 1.3 mg/100 ml concentration (165)

±6.6% at 0.1 mg/100 ml concentration (170)

±4% at 20.2 mg SO_3 /100 ml (160)

E. Interferences

BaSO_3 will precipitate along with BaSO_4 unless it is removed prior to precipitation. Other interferences result from the usual coprecipitation and occlusion problems associated with BaSO_4 precipitation (196,303).

F. Comments

The method has several drawbacks including the need for good control over the temperature, rate of BaCl_2 addition, amount and degree of agitation, and exact settling time after mixing before taking a turbidity reading. There is poor reproducibility between laboratories (see Precision and Accuracy above).

G. Conclusion

This method is not desirable as a result of its many inherent drawbacks.

5.5.2.6 Conductivity (161,162,337)

A. Description of Method

The conductivity of a solution containing H_2SO_4 is measured, and used to determine the sulfate ion concentration.

B. Areas of Application

Power plants (161,162,337).

C. Interferences

Conductivity is a non-specific method which will measure total solution conductance, hence any anion or cation other than H^+ ion from H_2SO_4 can be considered an interference.

D. Comments

Detailed consideration was not undertaken since conductivity is not a manual method. It is clearly necessary to confine this non-specific technique to closely controlled comparisons.

5.5.2.7 Precipitation Reactions (1,204,210,263,269)

A. Description of Method

A sulfate solution is precipitated as the barium or benzidine salt. The barium salt is filtered, dried, and weighed as $BaSO_4$ (1,263). The benzidine salt may be filtered, redissolved, diazotized and then coupled with an ethylene diamine derivative (269), or filtered, redissolved in a known excess of standard caustic and back-titrated with standard acid solution (76,204,210).

B. Areas of Application

Used in power plants (1,76,204) and for the determination of sulfate in waste water (269).

C. Applicable Concentration Range

Upper limit not given, micro determination by benzidine sulfate method reported down to 15 μg of sulfate.

D. Precision and Accuracy

One author claims 98-99% accuracy and 0.1% precision (269).

E. Interferences

The BaSO_4 method suffers from coprecipitation and occlusion of nitrate and chloride anions (196,303). Phosphate is reported to interfere in the benzidine sulfate procedure (269).

F. Comments

The methods are tedious and time consuming. Barium precipitation requires heating the sulfate solution while adding titrant and maintaining the solution at approximately 60°C for two or more hours while the precipitate digests. Benzidine sulfate is relatively water soluble and thus susceptible to losses during filtration.

G. Conclusions

The speed and accuracy (under field conditions) of this type of determination is poor compared to the colorimetric or titrimetric procedures.

5.5.2.8 Titrations Involving Ethylenediaminetetraacetic Acid (EDTA) (333,354)

A. Description of Method

In one variation (354), a known excess of a barium salt is added to a sulfate solution and the excess barium at pH 10 is titrated with an EDTA solution. Another variation is to precipitate BaSO_4 with BaCl_2 , filter the solution, and dissolve the precipitate in an excess of ammoniacal EDTA. The solution is titrated with a magnesium solution to an eriochrome T endpoint (333).

B. Areas of Application

Natural water analysis - boiler feed.

C. Applicable Concentration Range

Not given.

D. Precision and Accuracy

Accuracy of 92% at 20 ppm level, accuracy of 99% at 50 ppm level. Standard deviations for these levels are given as $\pm 1.4\%$ and $\pm 1.0\%$. Standard deviation at 200 ppm given as $\pm 3.4\%$ (354).

E. Interferences

Difficulties include interaction of EDTA with the barium sulfate precipitate, unsatisfactory behavior of the indicator, and changeable behavior of the EDTA-barium complex. pH control is also necessary (333).

F. Conclusions

This method is not as good as either the barium chloranilate or the thorin procedures.

5.5.2.9 Summary and Conclusion

In summary, our examination of the methods now being used for the measurement of sulfate ion concentration indicates:

A. Thorin and arsenazo III are the best indicators for a titration procedure since they provide good precision and accuracy, are not subject to major interferences (which cannot readily be eliminated) and may be applied over a wide range of concentration.

B. NaOH titration is non-specific and therefore not desirable for a very precise and accurate method.

C. Colorimetry using barium chloranilate is one of the best overall methods for the determination of sulfate.

D. Turbidimetry has many drawbacks which exclude it from further consideration.

E. Conductivity is non-specific in addition to not being within the scope of the present work.

F. Precipitation reactions have drawbacks such as coprecipitation which exclude them from further consideration.

G. Reactions involving EDTA have serious problems to overcome before being considered as useful.

The two methods of choice, therefore, are titration with barium using thorin (or other) indicator and the barium chloranilate colorimetric procedure.

5.5.3 Analytical Methods for the Measurement of Sulfite Ion Concentration

5.5.3.1 Iodine Titration by Decolorization of a Standard Iodine Solution (95,170,192,215,410,504)

(See Section 5.4.2.3.) A variation of iodine titration is to use excess iodine and titrate the excess with standard thiosulfate solution. All other comments in Section 5.4.2.3 apply here as well.

5.5.3.2 Iodine Titration of NaHSO_3 Solution (384)

A. Description of Method

A caustic solution containing NaHSO_3 is acidified, and titrated with a standard iodate solution. Glycerol (5%) is added to the caustic to prevent sulfite oxidation to sulfate during collection.

B. Area of Application

Sulfuric acid plants (384).

C. Applicable Concentration Range

No lower limit given; highest concentration stated is 0.9 gm SO_2 absorbed in 100 ml of 10% NaOH solution.

D. Precision and Accuracy

Accuracy is indicated to be 99.5%. Precision is about 1-2%.

E. Interferences

See Section 5.4.2.3.

F. Comments

The method uses the reaction $2\text{SO}_2 + \text{KIO}_3 + 2\text{HCl} \rightarrow 2\text{SO}_3 + \text{KCl} + \text{H}_2\text{O} + \text{ICl}$. Presence of some KI initially forms some iodine, which is observed in a chloroform globule in the bottom of the solution flask. The endpoint is observed by the disappearance of the purple color when an excess of KIO_3 is present. Vigorous shaking is necessary to maintain good precision. Only standard solution required is KIO_3 .

G. Conclusion

The major source of error is in the use of caustic for collection of the SO_2 .

5.5.3.3 West-Gaeke Colorimetric Determination of SO_2 (13,128)

A. Description of Method

Gas containing SO_2 is bubbled through a solution of 0.1M sodium tetrachloromercurate (TCM). The TCM reacts with SO_2 to form dichlorosulfitomercurate ion. Reaction of the ion with formaldehyde and acid-bleached pararosaniline dye forms a red-purple solution of pararosaniline methyl sulfonic acid. Concentration is determined by colorimetry.

B. Applicable Concentration Range

0.005-5 ppm.

C. Precision and Accuracy

Reported as $\pm 10\%$ from 0.005-0.10 ppm. Accuracy increases with concentration.

D. Interferences

O_3 interference can be eliminated by gas filtration through $FeSO_4$ crystals. NO_2 interference can be eliminated by the addition of sulfamic acid or o-toluidine to the collected sample before addition of formaldehyde and pararosaniline. Heavy metal interference is eliminated by addition of EDTA (ethylene diamine tetraacetic acid disodium salt) to the TCM solution.

E. Comments

Color stability is reported to be independent of temperature in the range of 11-30°C and to be stable for up to 3 hours.

F. Conclusion

The method appears well suited to the selective determination of SO_2 at ambient levels. Stack samples containing SO_2 concentrations higher than 5 ppm should be diluted down to 5 ppm or less to use this procedure. The SO_3 content of the sample after dilution would be extremely small, thus a second sample would be needed if an SO_3 determination is desired.

5.5.3.4 Acid Titration - $NaHSO_3$ Solution (204)

This is the method described by Berk and Berdick. The SO_2 is collected by bubbling through a standard NaOH solution. After a known volume of gas is bubbled through the solution, the excess caustic is titrated to pH 4.1 with standard acid. This method is subject to a number of interferences described in Section 5.4.2.4.

5.5.3.5 Conclusion

None of these techniques offers any advantage over oxidation of SO_2 and determination as sulfate.

5.5.4 Laboratory Investigation of Analytical Methods for Determination of Sulfate Ion

5.5.4.1 Titration of Sulfate Solutions with Barium Perchlorate

A. Screening of Indicators

Several indicators have been reported (394) to be superior to thorin for the titration of sulfate ion with barium ion. The main reason given for superiority over thorin is a more readily seen endpoint (better color change differentiation), and in the case of arsenazo, a claim is made for fewer interference problems. Of those reported, only three, Sulfonazo III, Methylsulfonazo III, and Arsenazo III, were available (Aldrich Chemical Co.).

Sulfonazo III and methylsulfonazo III are reported to change from wine-red to blue when barium ion is in excess. The solutions as prepared (0.1% in deionized water) were blue. Repeated attempts to produce a red color in the presence of sulfate failed, so that no further work has been done with these two indicators.

Arsenazo III is reported to give a red to blue endpoint color change (617). The blue color is due to the presence of lead ion in the titrant. We have prepared several bottles of arsenazo III solution and of the titrant as described in the paper by Fukui (617).

The dye is digested in water overnight, then filtered and the filtrate stored in a dark bottle. The titrant is a mixture of barium acetate and lead acetate in 80% isopropyl alcohol. We observe a purple endpoint, which is no easier to see than the thorin endpoint. A series of four titrations showed a coefficient of variation of 1.6% as compared to 0.5-0.7% for thorin. (See E following.) No further work has been done with this indicator-titration system. Of the indicators studied, thorin appears to be the best. (See below.)

B. Thorin Indicator

Solutions of 80% isopropanol containing 4 drops of 0.2% thorin indicator were titrated with 0.006 N $\text{Ba}(\text{ClO}_4)_2$

solution in 80% isopropanol to determine blank reproducibility and to observe the color change at the endpoint. The change is from yellow to pink and is reported by Fritz and Yamamura (303) to be quite sharp. We found the endpoint to be nebulous, the color going from yellow through orange to pink. Solutions containing known amounts of sulfate were used to standardize the $\text{Ba}(\text{ClO}_4)_2$ solution; the standard deviation of the titration of four samples was 0.6%.

Barium titrant concentrations of 0.005M have been recommended by Fritz. Nine titrations at this concentration yielded a precision (coefficient of variation $\equiv$ standard deviation $\times$ 100/mean) of 1.0%. Endpoint visibility was improved by addition of 1-2 drops of methylene blue solution (0.0125 g/100 ml water) in addition to the two drops of thorin.

However, remaining endpoint visibility problems suggested an increase in the titrant strength to 0.01M barium. At this concentration endpoint, detection becomes simple; a coefficient of variation of 0.5-0.7% is obtained. (See Section E following.) The 0.01M concentration is, therefore, recommended.

C. Effects of Solution pH on Thorin Titration

Samples were prepared at several apparent pH's by the addition of perchloric acid or 0.25M magnesium acetate to solutions of sulfuric acid in 80% isopropyl alcohol. Magnesium ion is claimed not to cause an interference in the precipitation reaction (345).

a. Procedure

1. Pipet $X\text{ ml } 0.0054 \text{ H}_2\text{SO}_4$ into a 100 ml beaker ($X = 5 \text{ or } 8$).
2. Add 40 ml isopropanol and dilute to 50 ml mark with H_2O . Adjust pH with dilute HClO_4 or 0.25M magnesium acetate.
3. Add 2 drops 0.2% thorin and 1 drop 0.0125% methylene blue.
4. Titrate to a pink endpoint using 0.01M barium perchlorate adjusted to pH 3.5 with dilute perchloric acid.

The results at two different sulfate levels are given below.

<u>Sulfate Level</u>		<u>ml Titrant Required</u>				
ml of 0.0054M H_2SO_4	pH	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
5		4.39	4.36	4.34*	4.23	4.17
		4.36	4.34		--	4.18
		4.36	4.35		4.11	3.88
8		2.77	2.76	2.77*	2.59	2.63
		2.82	2.81		2.59	2.58
		2.77	2.72		--	--

* Mean values obtained from precision experiments following.

The titration may, therefore, be conducted at pH's of 1, 2, and 3 with very little error. However, if the pH of the solution is 4 or more a negative error results. This is in agreement with the literature which states that thorin functions best at an apparent pH of 2 to 3, with a usable range of 1.5 to 3.5 (196).

D. Effect of Temperature on Thorin Titration

Samples were titrated with 0.01M barium perchlorate to a thorin endpoint after temperature equilibration at 20°C and 30°C. Solution temperatures rose and fell one degree at each temperature during the titration. Essentially no change in titer was observed. Data is as follows:

<u>20°C</u>	<u>30°C</u>
4.24 ml titrant	4.22 ml titrant
4.25	4.21
4.24	4.21

No temperature restriction is, therefore, necessary in the titration procedure.

E. Precision of Titration Using Thorin as Indicator

a. Procedure

1. Pipet X mls of 0.0054M H_2SO_4 into a 100 ml beaker (X = 5 or 8).
2. Add 40 ml of isopropyl alcohol and dilute to 50 ml mark with water, adjust pH to 3 with dilute HClO_4 or 0.25M magnesium acetate.
3. Add 2 drops 0.2% thorin and 1 drop 0.013% methylene blue.
4. Titrate to pink endpoint using 0.01M barium perchlorate adjusted to pH 3.5 with dilute perchloric acid.

b. mls of Titrant Required for X = 5
5 ml buret used

2.75	2.70
2.74	2.73
2.74	2.71
	2.70

mean value = 2.73

standard deviation = ± 0.02

cv* = $\pm 0.7\%$

c. ml of Titrant for X = 8
5 ml buret used

4.32	4.35
4.38	4.33
4.33	4.36
4.35	4.32
4.34	4.35

mean value = 4.34

standard deviation = ± 0.02

cv* = $\pm 0.5\%$

* coefficient of variation

F. Study of Potential Interferences in the Titration Procedure

A number of cations and anions have been reported to interfere in the titration of sulfate ion with barium ion. Presumably, cationic interference from particulates would be essentially nil if the particulate filter in the probe is working properly. However, a small cation exchange column, used in the procedure, would eliminate any cations which get by the filter or are carried through in the gas phase.

To simulate interferences for this experiment, we prepared solutions of a number of materials, then shook the solutions with at least 1 ml wet volume of Dowex 50W-X8 ion exchange resin to exchange the solution cations with the hydrogen ions on the resin. Aliquots of the solutions were then taken for use in the interference study.

a. Procedure

1. 50W-X8 resin washed with 3N HCl, then rinsed with distilled water until effluent showed no Cl^- when checked with AgNO_3 .
2. 1 + ml (wet volume) of the resin was added to 100 ml of potential interference at 0.2, 0.1, or 0.05M concentration (1% and 0.5% solutions of H_2O_2 were used).
3. Mixtures were shaken vigorously for at least one minute, then allowed to stand.
4. 5 ml aliquots of the anion solutions were pipetted into 100 ml beakers.
 - a. Add 5 ml 0.0054M H_2SO_4 .
 - b. Add 40 ml isopropanol.
 - c. Add 2 drops thorin + 1 drop methylene blue solution.
5. Titrate with 0.01M $\text{Ba}(\text{ClO}_4)_2$ to appearance of pink color.

The results obtained are given in the table below.

<u>Anion</u>	<u>mls. of Titrant at 0.1M</u>	<u>mls. of Titrant at 0.05M</u>
nitrate	2.08	2.49
fluoride	--	2.67 (2.03 at 0.2M)
chloride	2.38	2.45
bicarbonate	4.53	2.70 (very difficult endpoint to see)
phosphate	ppt.	ppt.
oxalate	ppt.	ppt.
formaldehyde	2.66	-- (2.65 at 0.2M)
hydrogen peroxide	2.65 (0.5%)	-- (2.66 at 1%)

Control was 5 ml H_2SO_4 + 5 ml H_2O + 40 ml isopropanol
2.66 ml of titrant
2.64
2.63

The most serious interferences are seen to be oxalate and phosphate ions. Oxalate ion was chosen to be representative of oxidized organic material. Phosphate was included in the list because it is known to be a serious interference to the determination of sulfate ion in streams and natural waters and if present in a stack-gas sample, could lead to considerable analysis error.

5.5.4.2 Determination of Sulfate by the Barium Chloranilate Method*

The pH of the chloranilate solution is a fundamental parameter which must be defined in the development of the color-metric method. As shown below pH 5.6 was selected as an optimum value. In this section the experimental basis for this selection is first described and followed by the description of method parameters at pH 5.6. Additional experimental work at other pH's is described in Part III, Activities Report.

* Additional laboratory work and discussion of this method is given in Appendix 3.

A. pH Dependence

Kanno et al (360) state that the absorbance of the chloranilate solution has a relatively strong pH dependence up to a pH of 5.2, but not at higher values. In order to compensate for variations in sample pH it is necessary to employ a buffer with capacity adequate to maintain absorbance within the desired limits. For this purpose, it is desirable to operate in the pH range which shows least absorbance sensitivity.

Kanno's findings have been checked on buffer solutions prepared from 0.2M sodium acetate and 0.2M acetic acid solutions. The results are shown below.

<u>pH</u>	<u>Absorbance vs H₂O</u>
4.6	0.505
5.2	0.462, 0.465
5.4	0.455
5.6	0.451
5.8	0.449, 0.449
6.0	0.443, 0.446
6.4	0.447
6.6	0.449
5.8	Blank 0.013

The developed color becomes relatively independent of solution acidity at pH 5.6. A sensitivity loss of ~ 10% occurs (from pH 4.6). Experimental optimization of other major factors (at pH 5.6) is described below.

B. Color Development as a Function of Mixing Time

Two experiments were performed to establish the minimum mixing time needed for color development to stop, or decrease to a barely discernible rate at room temperature.

All solutions contained:

5 ml of K_2SO_4 solution (2,500 ug/ml)

5 ml of pH 5.6 buffer

15 ml of sulfate-free water

25 ml of ethanol

0.2 gm of barium chloranilate

The solutions (except for 0 and 1-minute samples) were shaken on a Burrell Wrist-Action Shaker at the maximum rate obtainable. The 0-minute solution was simply swirled several times, then centrifuged. The one-minute solution was hand shaken for one minute at approximately the same rate as the solutions on the shaker. The results are indicated below:

Time (mins.)	Absorbance (vs H_2O)	
	Run 1	Run 2
0		0.394
1		0.455
2		0.459
5		0.462
10	0.462	0.470
15	0.463	--
20	0.471	0.475
25	0.468	--
30	0.471	0.478
60		0.480
15 (Blank)		0.028
30 (Blank)		0.029

A 20-minute mixing time was selected based on the above data.

C. Color Development as a Function of Temperature

Hand shaking of the solutions was necessary to avoid the awkwardness of thermostating the solutions while on the shaker. To determine relative efficiencies to samples were hand shaken for 20 minutes at room temperature and two samples machine

shaken for 20 minutes at room temperature. The absorbances obtained were as follows:

Hand Shaking

0.452

0.453

Machine Shaking

0.454

0.455

Having found that hand shaking was satisfactory, six samples were hand shaken in constant temperature baths, three at 20°C and three at 30°C. Measured absorbances on these solutions were:

20°C

0.449

0.450

0.452

30°C

0.460

0.460

0.459

Due to an oversight, the absorbances were not remeasured after the solutions reached room temperature. However, previous measurements suggest that the changes on reaching room temperature will be = 0.002 or 0.003; thus, temperature correction is not necessary if the sample and calibration curve solutions are mixed at a temperature differential of say 5°C.

D. Amount of Barium Chloranilate Required

Three similar solutions were prepared for mixing with only the amount of barium chloranilate differing. Total solution volume was 50 ml. Results follow:

GMS Barium Chloranilate

0.1

0.2

0.3

Absorbance vs H₂O

0.459

0.470

0.470

Thus, 0.2 gm of barium chloranilate appear sufficient to react with the sulfate present in the 50 ml volume.

E. Adherence to the Beer-Lambert Law at pH 5.6

The solutions were prepared from a stock solution of K_2SO_4 at a concentration of 2,500 $\mu g SO_4^{--}/ml$. Final concentrations in the range 25 to 450 $\mu g SO_4^{--}/ml$. The solutions were mixed on a shaker at room temperature for 20 minutes, centrifuged at highest speed attainable with an International centrifuge (clinical model) for 5 minutes, then read on a Beckman DU at 530 nm vs H_2O using 1 cm cells. The results are given below.

<u>Concentration (Final Solution)</u> <u>$\mu g SO_4^{--}/ml$</u>	<u>Absorbance</u>
25	0.078
50	0.117
100	0.199
250	0.468
350	0.647
450	0.980

The plot of these data show linear dependence of absorbance on concentration to at least a concentration of 350 μg sulfate/ml for solution of K_2SO_4 .

F. Buffer Capacity

The buffer capacity of the pH 5.6 sodium acetate-acetic acid buffer was determined by diluting known concentrations of H_2SO_4 to a fixed volume of 20 ml adding 5 ml of pH 5.6 buffer and measuring the pH of the solution. An apparent pH was also measured after the addition of 25 ml of ethanol to the sulfate-acetate solution. A duplicate set of solutions was prepared in volumetric flasks, barium chloranilate added and the absorbance measured after shaking and centrifuging. The results are given below.

Volume of 0.025M H_2SO_4	pH Before Adding Buffer	pH After Adding Buffer	"pH" After Adding Ethanol	Absorbance ^a
0 ml	5.6	5.6	6.6	0.023
1 ml	2.7	5.4	6.4	0.108
2 ml	2.4	5.2	6.2	0.199
3 ml	2.3	5.1	6.1	0.299
4 ml	2.1	5.0	5.9	0.396
5 ml	2.1	4.9	5.9	0.491
7 ml	2.0	4.6	5.6	0.719 ^b
10 ml	1.9	4.2	5.3	1.09 ^b

a Absorbances obtained from separate experiment performed in the same way.

b Not done at same times as 0.5 ml set.

A plot of absorbance versus ml H_2SO_4 does not deviate from linearity until the pH after buffering fell to 4.6. This correlates well with earlier work which showed absorbance sensitivity below pH 5 (Section A).

These results accentuate the need for good control of pH. Adjustment of pH prior to buffering the solution has, therefore, been included in the procedure.

G. Description of Proposed Method

The procedure used is as follows:

- a. A volume of solution containing sulfate ions is pipetted into a 100 ml beaker.
- b. Adjust pH to 5-6 with 0.2M sodium hydroxide.
- c. Add five ml of pH 5.6 buffer (0.2M sodium acetate to which is added sufficient 0.2M acetic acid to give a pH of 5.6).
- d. Total volume is adjusted to 25 ml with sulfate-free water.
- e. Add 2 ml of ethanol.
- f. Pour contents of beaker into 100 ml volumetric flask.
- g. Add 0.2 g barium chloranilate.
- h. Shake on wrist-action shaker for 20 minutes.
- i. Centrifuge in 15 ml centrifuge tubes at maximum RPM (or filter).
- j. Decant into 1 cm cells and measure absorbance at 530 nm vs H_2O .

H. Precision of the Analytical Method

Using the procedure described in H (except that K_2SO_4 at the 250 ug/ml level is used rather than H_2SO_4 and preliminary neutralization), we have generated the following precision data:

Absorbance vs H₂O for Ten Separate Runs

0.473	0.477
0.472	0.475
0.477	0.471
0.475	0.473
0.473	0.478

Average = 0.474

Standard Deviation (1σ) = 0.002

Relative Error = $\frac{0.002 \times 100}{0.474} = \pm 0.4\%$

I. Interferences in the Barium Chloranilate Method (pH 5.6)

a. Solutions of potential anionic interferences were prepared at 0.2M, 0.1M, and 1% (in case of H₂O₂) concentrations:

1. Procedure followed was:

- 5 ml K₂SO₄ solution.
- 5 ml potential interference.
- Adjust pH.
- 5 ml pH 5.6 acetate buffer.
- 25 ml ethanol and shake well.
- Dilute to 50 ml with water.
- Add 0.2 gm barium chloranilate and shake on machine for 20 minutes.
- Centrifuge 5 minutes.
- Measure absorbance in 1 cm cell at 530 nm vs H₂O.

b. Data

Material Added	Absorbance of Solution with Indicated Initial Concentration Level of Interference	
	0.2M	0.1M
KNO ₃	0.472	0.464
KCl	0.453	0.461
NaHCO ₃	0.495	0.478

Material Added	Absorbance of Solution with Indicated Initial Concentration Level of Interference	
	0.2M	0.1M
K_3PO_4	1.43	0.685
$Na_2C_2O_4$	--	0.875
CH_2O	0.468	0.465
H_2O_2	0.473 (1% solution)	0.468 (1% solution)
NaF	not done	not done
$NaHSO_3$	0.810	0.865
K_2SO_4 references:		
run 1 -- (0.2M solutions)	0.517*	
run 2 -- (0.1M solutions)	0.508*	

* Prior runs out of the same batch of K_2SO_4 solution consistently gave 0.470 as absorbance. No reason is known for the different value observed here.

Again as with the titration procedure, oxalate and phosphate are the two largest interferences.

6. STATISTICS OF FIELD SAMPLING AND ANALYSIS

6.1 Introduction

In this section we discuss analytical errors in general terms and summarize the scattered literature references, as well as some heretofore unpublished data on the precision and accuracy of the analytical and sampling procedures, separately or combined, depending upon the source material. Finally we analyze in some detail the few comparative evaluations of methods conducted as field trials.

The statistical analyses presented in this section have been simplified in order to obtain suggestive results rapidly. For example, the linear regression model employed here assumes that no portion of the error is attributable to the independent (x) variable, although more realistic models are available (532) and will be utilized in future work where desirable. We believe this procedure is justifiable for qualitative results in a field where such comparisons have been conspicuously absent.

6.1.1 Accuracy

In most manual methods, the pollutant of interest is first trapped and then made to reduce or oxidize another species, react to form a color, act as an acid or base, etc. Because these are all general, class or type, reactions it is difficult to obtain specificity and eliminate side reactions and/or interferences with other species which lead to a loss in accuracy. This is particularly true for highly labile species where there is opportunity for the gas to react before an analysis can be completed. An ultimate but not necessarily attainable, goal of the analytical chemist is the use of a method which will not disturb the system during measurement and which will provide complete specificity.

Another factor which makes the accuracy of manual (or instrumental) techniques not generally predictable is the wide range of matrices encountered in combustion processes. To properly evaluate accuracy one must carefully assess each matrix to which the method is

to be applied. One hopes for and expects high accuracy but in practice 90-95% is reasonable for field sampling work.

It is very difficult to determine the accuracy of a method in the field. However, a few workers have correlated stoichiometric SO_2 concentrations calculated from the sulfur content of the fuel with measured SO_2 concentrations. If we assume that sulfur emission is quantitative, we can use this technique as a measure of the accuracy under field conditions. This approach is discussed in Section 6.4.

6.1.2 Precision

Many factors contribute to imprecise results. These include reaction chemistry, operator errors, and equipment variability. Various steps in the overall procedure, including aliquoting, dilutions to the mark, etc. each add to the imprecision. Techniques which depend upon spectrophotometric read-out will have an inherent imprecision of up to several percent (for a simple analytical instrument) resulting from the inability of the operator to read the absorbance dial to any higher precision. In addition to these factors there exist problems associated with sample collection and sample instability and, finally, those of interlaboratory variations.

Ultimately, the desired precision of the mean, which is a function also of replication, must be related to the resources allocated and optimization of the total emissions determination program.

6.2 Precision Obtainable in Field Sampling of Sulfur Oxides

Since the following data were obtained at power plants, the accuracy of the methods involved was not determined in an absolute sense. However, the precision (sampling and analysis combined) of these methods observed under field conditions, can be computed from replicate measurements.

We have made some recent measurements of SO_2 and SO_3 concentrations at an oil-fired power plant (516). The sampling system and

procedures were similar to those used previously (527) except that electrically heated probes and sampling lines were used. SO_3 was collected in midget impingers containing 80% isopropanol; SO_2 was collected in midget impingers containing 3% hydrogen peroxide. The barium chloranilate method was used for analysis of both SO_2 and SO_3 . In five consecutive tests, we obtained a coefficient of variation (standard deviation $\times$ 100/mean) for SO_3 (sampling and analysis) of $\pm 11\%$ (at 10 ppm). The coefficient of variation for the SO_2 measurement (sampling and analysis) was considerably better, $\pm 2.6\%$ (at 1500 ppm). Seidman (78) obtained a coefficient of variation of 1.5% for 33 SO_2 samples (sampling and analysis) collected in peroxide and analyzed by barium titration using thorin indicator, in good agreement with the precision of our colorimetric analyses.

Corbett (347) utilized 80% isopropanol (IPA) absorption for SO_3 and peroxide collection for SO_2 with turbidimetric readout (160) for both. Data were obtained from about 30 tests run in duplicate at an oil-fired power plant. Corbett's values for the standard deviations were used directly. We have computed the mean SO_x concentrations and the coefficients of variation for the duplicate samples only. The results are given below:

Species	Mean SO_x	Standard Deviation, ppm	CV%
	Concentration, ppm		
SO_2	997	73.3	7.4
SO_3	12.2	2.6	21.4

The coefficient of variation for SO_2 and SO_3 includes sampling errors as well as source variation. The more severe sampling problem for SO_3 is reflected in the much larger value of its coefficient of variation. The large values of the coefficients of variation for SO_2 and SO_3 are presumably a result of the imprecise analytical method (turbidimetry).

ESSO Research Ltd. (520) has done a statistical analysis of field data for SO_3 determined by collection in 80% isopropanol and analyzed by turbidimetry. They obtain a standard deviation of 2.8 ppm SO_3 for the total method (sampling and analysis) of which the error due

to the analytical method contributes (0.6 ppm, and sampling error 2.7 ppm). Thus the larger contribution to the total error is in sampling. If we assume a mean of 15 ppm SO_3 (for oil-fired combustion) the total coefficient of variation becomes $\pm 19\%$, in good agreement with Corbett's observations.

Nine duplicate SO_3 samples obtained at a coal-fired power plant collected in NaOH and analyzed by the benzidine method (548) show the same precision as that obtained with isopropanol collection and turbidimetric readout, $\text{CV} = \pm 19\%$ at a mean SO_3 concentration of 61 ppm. Significantly, however, the mean SO_3 concentration (61 ppm) for NaOH collection* is considerably higher than the 10-30 ppm range usually obtained at large fossil fuel fired plants. Gillham has compared measurements of SO_3 collected in distilled water and caustic solution and found that caustic (NaOH) collection produced SO_3 results which were nearly twice as high as the aqueous acid collection method for SO_3 . This bears out our earlier conclusion (Section 3) that stabilization of sulfite ion is a major problem in caustic collection of SO_3 .

We have obtained unpublished field data from Combustion Engineering (498) on determinations of SO_3 collected by the controlled condensation method, and SO_2 , collected in peroxide. Analyses were performed by titration with standard NaOH solution using bromphenol blue indicator. The data were obtained at an oil-fired plant during dolomite addition tests. We have grouped the SO_3 data (27 tests run in triplicate) into high and low SO_3 concentrations ranges and calculated the precision statistics given in Table 6-1 below.

* Both SO_2 and SO_3 are collected together, leading to the possibility of oxidation of sulfite and consequent poor precision and accuracy in the sulfate analysis.

TABLE 6-1
PRECISION STATISTICS FOR SO₃ BY CONTROLLED CONDENSATION METHOD

No. of Triplicates *	Mean SO ₃ Conc. (ppm)	Std. Dev. (ppm)	CV%
10	5.7	0.36	6.3
16	12.2	0.49	4.0

* 1 set discarded

Combustion Engineering conducted 20 SO₂ tests with three or more replicates. These data were also grouped into high and low concentration ranges. The calculated precision statistics are given in Table 6-2 below:

TABLE 6-2
PRECISION STATISTICS FOR SO₂ BY PEROXIDE COLLECTION

No. of Tests	Total No. of Runs	Mean SO ₂ Conc. (ppm) and Range	Pooled Std. Dev. (ppm)	CV%
9	30	664 (580-890)	35.0	5.3
11	33	1100 (930-1170)	24.2	2.2

The decreased precision at the lower SO₂ concentration is significant. Above 1000 ppm the precision is comparable to that obtained with methods specific for sulfate, and in good agreement with the precision of ±2% reported by the Bay Area APCD (145) for this method. The poorer precision at the lower SO₂ concentration is probably due to interferences from acidic species in the flue gas. The Japanese Industrial Standard (430) does not recommend use of standard NaOH titration for

SO₂ collected in peroxide at concentrations below 500 ppm because of this problem. Thus, NaOH titration has a limited range below which it should not be used if accurate results are expected.

In general non-specific analytical methods for sulfate, such as the iodine method (see following) or peroxide collection followed by NaOH titration, may provide results of good precision at high SO₂ concentrations but lose precision at low SO₂ concentrations, where interferences appear to become significant. We have not yet located any results at low SO₂ concentrations for peroxide collection followed by analysis by the barium chloranilate or barium ion titration. We may, however, utilize Corbett's (347) work which employs an imprecise method specific for sulfate (turbidimetry). Selecting only the SO₂ concentrations below 1000 ppm we obtain the following statistics:

<u>No. of Duplicates</u>	<u>SO₂ Conc. Range (ppm)</u>	<u>Mean SO₂ Conc. (ppm)</u>	<u>Pooled Std. Dev. (ppm)</u>	<u>CV%</u>
14	200-900	685	52	7.6

Comparison of these statistics to those for the complete range of Corbett's work presented previously (p. 156) reveals that, although the mean SO₂ concentration was reduced from 997 ppm, the coefficient of variation remains essentially constant (7.6 compared to 7.4%). The conclusion of this indirect argument is that methods which are specific for sulfate appear to provide nearly the same precision over a broad range of SO₂ concentrations, although non-specific methods yield poorer precision at low SO₂ concentrations.

Sulfur Oxide statistics reported by the British Standards Institute are given in Table 6-3 (379).

SO₂ is determined by collection in standard iodine solution and measurement of the volume of gas required to decolorize the solution. SO₃ is collected in 80% isopropanol and titrated with BaCl₂ using thorin indicator.

TABLE 6-3
BSI SULFUR OXIDE STATISTICS

Sulfur dioxide

Standard deviation (10 results): 10 ppm at 200 ppm by volume
20 ppm at 2000 ppm by volume

Accuracy: +5 percent at 200 ppm by volume
±5 percent at 2000 ppm by volume

Sulfur trioxide

Standard deviation (10 results): 0.2 ppm at 5 ppm by volume (169)
0.2 ppm at 20-50 ppm by volume

Accuracy: +10 percent at 5 ppm by volume
±5 percent at 20-50 ppm by volume

Lower limit of detection: 0.5 ppm by volume

The standard deviation cited for SO_3 at 5 ppm in the BSI document (374) appears to be in error and is corrected above. The source cited by BSI, Fielder and Morgan (169) give the standard deviation (of the analytical method alone) for 5 ppm (equivalent) SO_3 as 0.2 ppm (not .02 ppm as given in reference 379).

At 2000 ppm SO_2 , the iodide-iodine method has a reported standard deviation of 20 ppm yielding a coefficient of variation of 1%. This is the error in determination of the total volume (reported as ±5 sec for a 10 minute run, reference 170). The "accuracy" (not defined) stated as ±2% may include factors not explicitly stated. At 200 ppm SO_2 , the coefficient of variation becomes 5%, which is stated "accuracy". Although it is clear that accuracy and precision should decrease at lower concentration, these results are not self-consistent, since no additional factors appear in the "accuracy" at low concentrations. As a result of the vague definitions employed and apparent inconsistencies, we cannot properly evaluate these data. It is difficult to accept the

results at 2000 ppm SO_2 as representative of the precision to be expected for a non-specific method subject to many interferences.

For SO_3 the value given for "accuracy" probably represents the errors in sampling and analytical methods combined. If this is true, the value obtained at 5ppm SO_3 ($\pm 10\%$) is in good agreement with our results ($\pm 11\%$) using the barium chloranilate method.

Data on SO_2 collection by absorption in NaOH was obtained at a coal-fired power plant (548). The NaOH solution, after collection, was divided into three aliquots. Each aliquot was analyzed by a different analytical method. The methods used were the benzidine, the modified Shell* (barium ion titration with thorin indicator), and the Berk and Berdick. These methods have been described in detail by Smith et al (76). The mean SO_2 concentrations as well as the coefficient of variation for each analytical method are given in the table below for aliquots of 5 duplicate samples.

TABLE 6-4
COMPARISON OF ANALYTICAL METHODS FOR SO_2 AFTER CAUSTIC ABSORPTION

Analytical Method	Mean SO_2 Conc. (ppm)	CV%
Benzidine	1362	6.8
"modified Shell"	1356	5.3
Berk & Berdick (HCl titration with bromphenol blue indicator)	1780	3.3

*The sample is collected in caustic rather than peroxide, and subsequently oxidized.

The most precise analytical results for caustic scrubbing are apparently obtained with the Berk and Berdick (B&B) method. However, the mean SO_2 concentration obtained by the B&B method is 30% higher than the SO_2 concentration obtained by either of the other two techniques. We point out again that these are analyses of aliquots of the same NaOH solution and should yield identical results for all three methods. These results suggest that the accuracy of the B&B method is quite poor, at least in this case.

Another significant feature of the above results is that the modified Shell method gives a coefficient of variation of 5.3% compared to 1.5% [results of Seidman (78)] when peroxide collection is used. This again emphasizes the importance of the collection medium.

6.3 Comparison of Sampling Errors and Analytical Errors in the Determination of Sulfur Oxides

In the previous section, the precision of both sampling and analysis was combined. It is of interest to know the magnitude of error in each component (sampling and analysis) in order to minimize the error in each process. Sampling and analytical errors can be resolved by determination of the errors due to the analytical method only and assuming that all other errors are due to sampling.

The combined sampling and analytical error (precision) for 80% IPA absorption with analysis by the barium chloranilate is $\pm 11\%$ (Section 6.2). The analytical error for the barium chloranilate method is $\pm 4\%$ at 10 ppm SO_3 (516). We may determine the error in sampling only from the difference between the total CV and the CV due to the analytical method as follows:

$$(CV_S)^2 = (CV_T)^2 - (CV_A)^2$$

$$(CV_S)^2 = (11)^2 - (4)^2$$

$$CV_S = 10\%,$$

where CV_S is the coefficient of variation attributable to sampling precision. The largest fraction of the error (87%) is due to sampling.

The precision (sampling and analysis) of the controlled condensation collection method for SO_3 is considerably better ($CV = 6\%$) than 80% IPA absorption.

Since the error in the analytical method (NaOH titration) is about the same as colorimetric analysis, we have:

$$(CV_S)^2 = (6.0)^2 - (4.0)^2$$

$$CV_S = 4.5\%$$

The collection method is, thus, an important factor in the overall reliability since the sampling error in the 80% IPA absorption method is nearly twice the sampling error for the controlled condensation method. This reduced error for SO_3 collection by controlled condensation is not surprising since the problem of oxidation of dissolved SO_2 is eliminated.

The precision of the barium chloranilate analytical method for SO_2 determined from duplicate analyses of aliquots of 23 stack samples (516) is $\pm 2\%$ (at an absorbance of 0.5). The coefficient of variation found for SO_2 sampling and analysis was $\pm 2.6\%$. If we assume no source variation we may estimate the error in SO_2 concentration resulting from sampling from these values as follows:

$$(CV_T)^2 = (CV_A)^2 + (CV_S)^2$$

$$(2.6)^2 = (2.0)^2 + (CV_S)^2$$

$$(CV_S) = 1.3\%$$

Thus, if 2% of the total error is due to the analytical method, 1.3% can be attributed to the sampling error for SO_2 . This result is not unexpected in view of the high concentration of SO_2 and the quantitative collection of SO_2 in hydrogen peroxide. For peroxide collection followed by barium ion titration with thorin indicator we obtain 1.5% for CV_T and 1.0% for CV_A ,* whence CV_S for this method is 1.1%, in good agreement with the results above. The sampling error for SO_2 is comparable to the analytical error, in contrast to SO_3 determination by absorption.

6.4 Comparison of Stoichiometric to Measured SO_2 Field Results

We have located two sets of data for which stack analyses have been systematically compared to SO_2 flue gas concentrations estimated from the sulfur content of the fuel. These data may be used to estimate the accuracy of various methods in field sampling. Unpublished data on a comparison of SO_2 analytical results conducted in 1963 at a coal-fired utility boiler by NAPCA personnel using the Shell Development Method, have been furnished by R. Larkin of NAPCA (548). Stoichiometric sulfur dioxide values were determined from total volumetric flow and sulfur content of the fuel.

To obtain a measure of the accuracy of the Shell method, we have conducted a simple regression analysis of the Shell data (10 points) versus the stoichiometric values, taken as the dependent variable. This procedure is, of course, as dependent upon the accuracy of the calculation as upon the method of analysis. (See footnote, Section 6.2.)

The regression equation obtained is:

$$Y_{st} = 40 + 0.86 X_S$$

*NAPCA data on 12 aliquots of SO_2 stack samples (548).

$$\bar{Y}_{st} = 1108 \text{ ppm}$$

$$SE = 79 \text{ ppm}$$

$$CV = 7.1\%$$

A scatter diagram for the data and the regression equation (solid line) are shown in Figure 6-1. The relatively low value of the coefficient of variation is encouraging in view of the severe sampling problems encountered in a coal-fired utility.

6.5 Conclusions

SO₃ collected by absorption in a liquid is relatively imprecise (and inaccurate) as a result of oxidation of dissolved SO₂. The coefficient of variation observed is in the range ±10-20% (sampling and analysis) depending on the analytical method. The controlled condensation method, which eliminates the problem of oxidation of dissolved SO₂, yields considerably better precision. The coefficient of variation for this technique was found to be ±5% for sampling and analysis. The controlled condensation method is the most precise and/or accurate collection technique for SO₃ from fossil fuel combustion sources.

Caustic collection for SO₂ yields poor precision presumably as a result of scrubbing of interfering flue gas components. With barium ion titration and thiorin indicator, a coefficient of variation of 1.5% (sampling and analysis) is achieved for peroxide scrubbing of SO₂. Caustic scrubbing followed by barium ion titration yields considerably poorer results, CV = 5.3% (sampling and analysis). Since the analytical method is the same, caustic scrubbing techniques do not appear attractive. The iodine-iodide scrubbing solution technique lacks the necessary quantitative field data for assessment and the many probable interferences preclude its selection as a precise and accurate method for combustion sources. Peroxide collection is the most widely used technique because the interferences are minimal and it yields precision better than ±3% in field use. NaOH titration coupled with peroxide collection provides good precision (CV = 2.2%) at high (1100 ppm) SO₂ concentrations, but at lower concentrations the precision is considerably poorer (CV = 5.3%, at 664 ppm SO₂).

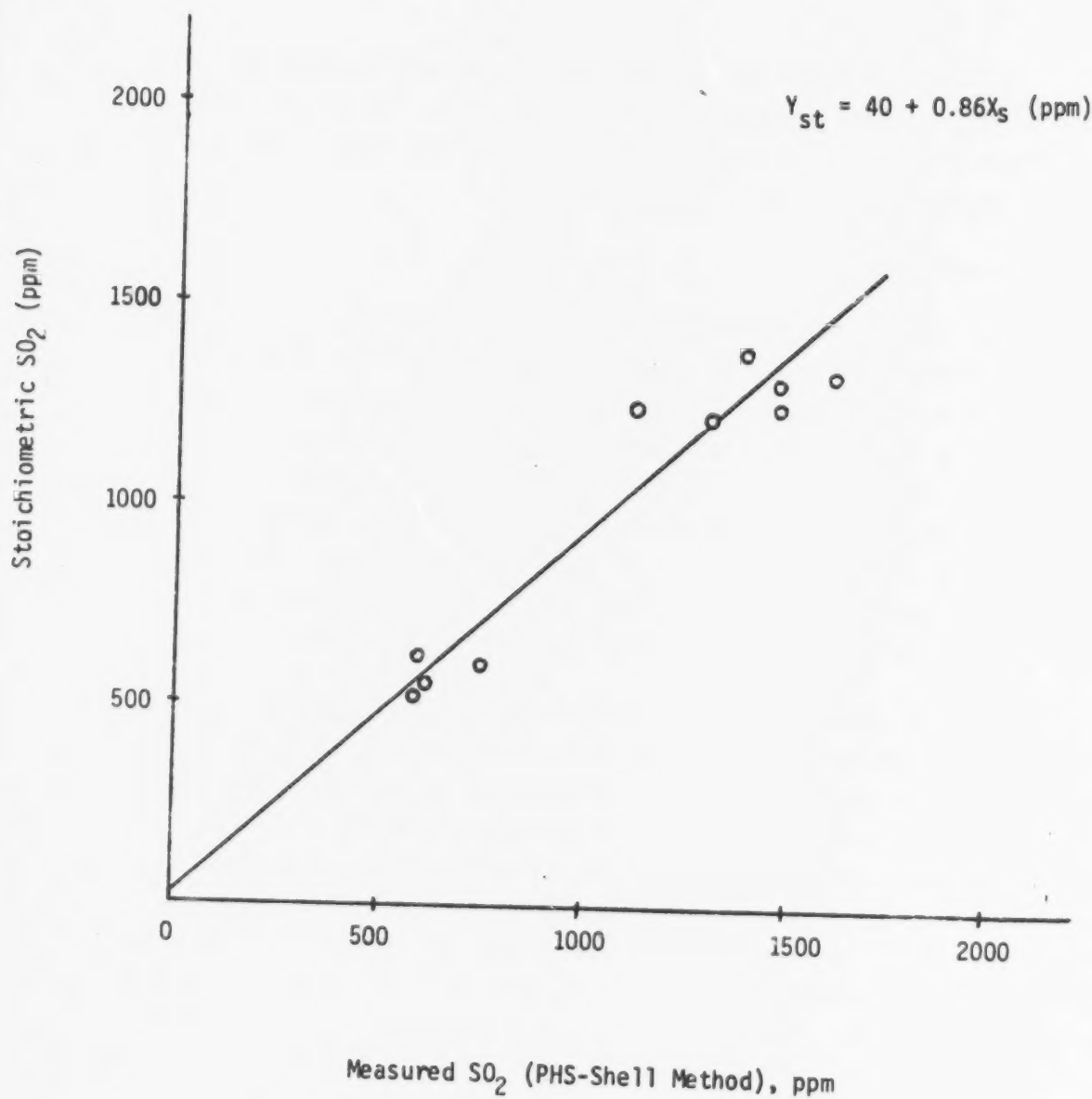


Figure 6-1. Comparison of Stoichiometric (calculated) to Measured SO_2 Concentrations (coal-fired boiler)

This is characteristic of a non-specific method for sulfate determination.

The accuracy of the best field methods for SO_2 as judged by crude comparison to limited stoichiometric calculations apparently falls in the range of 3-8%. Subjective evaluation suggests 5 to 10% as the range to be expected in the emission determination for SO_2 at ≥ 1000 ppm.

There is as yet no basis for determining the accuracy of SO_3 field measurements.

7. RECOMMENDED METHODS

7.1 Collection Methods for SO₃

Our objective is the selection of (manual) collection and analytical procedures which will give the highest possible precision and accuracy for SO₃ in the range 5 to 10-300 ppm. It is thus important to choose a system with a high (and therefore, reproducible) collection efficiency. The controlled condensation technique has been shown to have a high collection efficiency in several different configurations (80, 81, 403, 411). The primary basis of selection is, however, the observed greatly improved precision of the controlled condensation method compared to IPA absorption techniques.

A number of objections have been expressed to the field use of the condenser method. These include:

1. Difficulty in maintaining temperature
2. Filter plugging
3. Fragility of equipment
4. Possible failure in dry process streams

The first objection may be overcome by using a constant boiling liquid in the condenser. The only auxiliary equipment needed in this case is a heating tape, eliminating the need for a temperature controller and thus improving equipment portability. Combustion Engineering uses a simple thermostat for temperature control. The second problem is of a major consequence since the important coal-fired plants produce an effluent with high particulate loading. Redesign of the sampling probe to divert the larger particles* would reduce the particulate loading on the filter. A quartz or pyrex pre-filter is satisfactory for most situations. The third objection can be solved by using a stainless steel jacket around the condenser (80, 502). The last problem

* For example, to include a miniature cyclone.

does not, of course, apply to combustion flue gases for which the condenser technique was developed. For dry process stream SO_3 measurements, the Flint technique should be compared to condenser methods at low temperatures.

On the basis of the preceding, we rate collection methods for SO_3 in the following order:

1. Controlled Condensation
2. Absorption in 80% Isopropanol

Other methods are either unsatisfactory or untested. A complete sampling system which may be used for either method is described in Appendix 4.

7.2 Collection Methods for SO_2

The most widely used collection methods for SO_2 have been based upon aqueous scrubbing media. Solid sorbents appear to have potential for development as specialized collection techniques, but no directly useable experimental data have yet been obtained. Dilution methods are inherently complex and offer no obvious advantages.

Three major aqueous media have been widely used in fossil fuel effluent collection, viz. peroxide, caustic and iodine. The remaining aqueous media utilized primarily in kraft mills and ambient sampling all present numerous problems and few advantages for fossil fuel use.

Both caustic and iodine collection methods have been shown to be subject to interference resulting in poor precision, particularly at low concentrations and/or in a "dirty" environment.

Collection in hydrogen peroxide is the most widely used technique and yields the best precision in field use. An additional advantage is that any sulfate method may be used for analysis as a result

of the ease of peroxide decomposition. Peroxide collection is clearly the method of choice for SO_2 .

A sampling system for SO_2 collection is described in Appendix 4.

7.3 Analytical Methods

The barium chloranilate method, and the $\text{Ba}(\text{ClO}_4)_2$ titration with thorin (or related) indicator provide the greatest selectivity and highest accuracy and/or precision for manual methods of sulfate analysis.

The major difficulty of the titrametric method using thorin indicator is the poor endpoint detectability. A number of different indicators have been tested but it is not clear that they offer significant improvement. Endpoint detectability may be improved by photometric readout (169,352).

The barium chloranilate technique is recommended because it eliminates the need for subjective judgement on the part of the operator, is relatively rapid, and can be applied over a wide concentration range. The Shell Development method (barium ion titration) is recommended as a result of the good statistical correlation observed in field tests, where experienced analysts are available. Detailed procedures for both methods are appended.

Analyses based upon determination of sulfite ion are not as desirable as sulfate methods. Even the West-Gaeke procedure for low concentrations of SO_2 , which offers the advantage of specificity, cannot be advantageously applied to combustion effluent analysis as a result of the complexity of the required apparatus and poorly understood interferences.

7.4 Simplified Methods

A simplified procedure may be obtained by determination of total SO_x in peroxide by elimination of the SO_3 scrubber. This technique

has been utilized by B.S.I. (618). There are intriguing possibilities for development of simplified SO_x methods based upon reaction with reactive solid sorbents such as alkali carbonates or supported oxidants such as MnO_2 on alumina. Indicating silica gel (detector tubes) also appear promising if proper controls are maintained.

A simplified procedure for the determination of SO_x by collection in peroxide followed by determination of total acidity is appended.

7.5 Correlation of Combustion Source Type with Selection of Sampling and Analysis Techniques

The selection and application of the recommended methods for sampling and analysis for the oxides of sulfur in stationary fossil fuel combustion sources is generally straightforward since a single method is applicable to all sources for a given contaminant. On the other hand, relatively high level R&D planning is required in some instances, e.g., the ab initio determination of SO_2 emissions from a large furnace with maximum precision and accuracy.

The principal factors to be correlated are:

1. The precision and accuracy sought
2. The concentration of the species sought
3. Source size
4. Transients

The precision and accuracy sought while primarily mission-oriented will determine the selection of method, i.e., precision or simplified. Should emission standards be set in terms of permissible lbs/hr, large sources will require higher precision analyses than small sources.

The major source factors proper are related to species concentration and operating transients. Species concentration, taken in the

general sense, here, includes spatial and temporal variance. As shown in Section 1.0, the primary interest for emissions determination is in relatively large sources. Thus, the special problems of small sources have been treated only briefly.

Gross species concentrations (SO_2 , SO_3 and SO_x) are of primary importance for determination of sampling duration in order to obtain a sample size adequate for the precision sought. For SO_2 and SO_x , simple stoichiometric calculations (see procedures) allow a priori determination of sampling duration required for desired sample size. For SO_3 sampling in high sulfur environments (residual oil and coal fired) a safe rule is to assume that 1% of the calculated SO_x will appear as SO_3 since experience shows this to be a lower bound in well controlled combustion at low excess air. Should sampling duration become inconveniently long, the various high sensitivity options of the barium chloranilate procedure may be applied. The IPA-thorin procedure is not recommended for low SO_3 concentrations for this reason. Neither SO_3 procedure has been designed for low sulfur (distillate fuel oil) sources since this application is remote.

A distinction in the dispersion of a population of SO_2 measurements may be expected between coal and residual oil-fired sources if the samples are taken for short periods (say 15 minutes) over an interval of hours. This results from the greater short term variance of the sulfur content of coal compared to the more homogeneous residual oil supply (Section 4.2.5). A high precision emission determination for a coal-fired source may, therefore, require either flue gas sampling over an extended period (week) or correlation of short term samples with representative (as burned) coal samples. Where such coal sampling and analysis is feasible, it is recommended as a simpler procedure than long-term flue gas sampling.

8. CONCLUSIONS

The primary conclusion that may be drawn from this analysis of high precision manual sampling methods for SO_2 and SO_3 is that the statistical basis for evaluation of existing methods is fragmentary, but reasonably self-consistent. The best present methods for SO_2 analysis, in the usual range of concentration, i.e., 500-2500 ppm, appear capable of yielding a precision of $\pm 3\%$ in stack analysis. The accuracy of these determinations should approach $\pm 5\%$, but the statistical basis for this value is yet weak. Peroxide collection methods for SO_2 appear best; caustic scrubbing is clearly the poorest major technique. The barium chloranilate analysis for sulfate should provide a major improvement in the elimination of the judgment error associated with the barium ion titrations of precision.

Analysis for SO_3 , in the usual range of interest, 10-50 ppm, is considerably more difficult and less precise than that for SO_2 , as is generally known. For IPA absorption, precision of the determination is generally in the range 10-20%. The condenser method provides considerable improvement in precision. Precision of $\pm 5\%$ at 10 ppm SO_2 has been obtained.

It is recommended that considerable effort be devoted to collection of significant sampling and analysis statistics for improved methods.

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APPENDIX 1
REFERENCE DATA ON THE COMBUSTION EFFLUENT ENVIRONMENT

Contents

1. Coal: Large
2. Coal: Intermediate
3. Coal: Small
4. Oil: Large
5. Oil: Intermediate
6. Oil: Small
7. Gas: Large
8. Gas: Intermediate
9. Gas: Small

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SIZE CATEGORIES FOR STATIONARY COMBUSTION SOURCES

	<u>Large</u>	<u>Intermediate</u>	<u>Small</u>
BTU Per Hour	$\geq 5 \times 10^8$	$3 \times 10^5 - 5 \times 10^8$	$< 3 \times 10^5$
Boiler Horsepower	$\geq 15,000$	10-15,000	<10
Pounds of Steam Per Hour	$\geq 500,000$	350-500,000	<330
Megawatts	≥ 50	<50MW	Not Applicable

LOAD (#/hr)	U	1,100,000	875,000
VELOCITY OR VOLUME	>110,000 cfm		
TEMPERATURE (°F)	275-475°F	255-280	250-260
O ₂ (%)	<25% XS	6.1-7.1 (41-50% XS)	5.2-6.0 (34-40% XS)
CO ₂ (%)		12.1-12.4	12.5-13.9
CO	0.02#10 ⁶ BTU(e) 0.5#/T (f)	8-25 ppm	0-10 ppm
SO ₂	38S#/T (f)	1450-2240 ppm	1370-2350 ppm
SO ₃		14 ppm	2-16 ppm
NO	20#/T (f)	650-1460 ppm 1.1-2.6 #/10 ⁶ BTU	520-664 ppm
NO ₂		100-1400 ppm 0.17-2.5 #/10 ⁶ BTU	
HC	0.007#/10 ⁶ BTU(e) 0.2#/T (f)	10-20 ppm	2-8 ppm

PARTICULATE

CYCLE & TRANSIENTS

REMARKS

e = estimating factor
f = emission factor

several boiler designs

SOURCE

552

470,471 cited
552

469

74

74

FUEL: COAL
SIZE: LARGE

LOAD (#/hr)

960,000

700,000
(75%)

830,000
(75%)

640,000
(75%)

full load
(partial load)

VELOCITY OR
VOLUME

TEMPERATURE (°F)

279-284

241-264

220-250

240-248

O₂ (%)

4.6-4.9
(28-30% XS)

4.2-4.5
(27% XS)

6.6-7.4
(45-53% XS)

5.8-5.9
(37-38% XS)

CO₂ (%)

14.3-14.4

14.6-14.8

11.9-12.5

12.8-13.3

CO

8-30 ppm

4-5 ppm

0.005-0.44
#/10⁶ BTU

SO₂

620-1470 ppm
(different fuels)

600-1300 ppm

1100-1820 ppm

SO₃

11-13 ppm

10-13 ppm

6-14 ppm

19-22 ppm

NO

397 ppm

304-346 ppm

125-217 ppm

386-521 ppm

0.38-2.5#/10⁶
BTU (0.28-1.9
#/10⁶ BTU)

NO₂

HC

13-14 ppm

6-8 ppm

0.001-10#/10⁶
BTU
no load data

PARTICULATE

CYCLE &
TRANSIENTS

REMARKS

SOURCE

74

74

74

74

22 cited in 552

FUEL: COAL	
SIZE: LARGE	
LOAD (#/hr)	150-000-1,100,000
VELOCITY OR VOLUME	
TEMPERATURE (°F)	
O ₂ (%)	10-34% XS
CO ₂ (%)	
CO	0-110 ppm (1 value @ 780 ppm)
SO ₂	
SO ₃	0.1-4.1% of S as SO ₃
NO	
NO ₂	
HC	
PARTICULATE	
CYCLE & TRANSIENTS	
REMARKS	
SOURCE	464
	378

FUEL: COAL
SIZE: INTERMEDIATE

LOAD (#/hr)	U	149,000#/hr (full)	108,000#/hr (75% load)	0.3-147x10 ⁶ BTU/hr
VELOCITY OR VOLUME	≤110,000 CFM			
TEMPERATURE (°F)	425-750	305-310	301-316	
O ₂ (%)	25-75% XS	4.5-6.6 (25-45% XS)	6.3-6.7 (42-46% XS)	
CO ₂ (%)		11.8-14.1	12.2-12.5	
CO	0.1#/10 ⁶ BTU(e) 3-50#/T (f)			<0.1-0.51#/10 ⁶ BTU
SO ₂		1260-1580 ppm	1530-1840 ppm	
SO ₃	38S#/T (f)	9 ppm	6-10 ppm	
NO				
NO ₂	8-20#/T (f)	329-393 ppm	308-347 ppm	0.30#/10 ⁶ BTU
HC	0.05#/10 ⁶ BTU(e) 1-10#/T (f)			0.005-0.1#/10 ⁶ BTU
PARTICULATE				
CYCLE & TRANSIENTS				
REMARKS	(e) = estimating factor (f) = emission factor		partial load	
SOURCE	552	74	74	468

FUEL: OIL
SIZE: LARGE

1000 BHP
Load factor 85% (usual)

LOAD (#/hr)

Usual Range

Recommended

Extreme Range

175 MW

VELOCITY OR
VOLUME

TEMPERATURE (°F)

O₂ (%)

CO₂ (%)

CO

0.3 ppm
0.005#/1000#

0- 100 ppm
0- 1.7#/1000#

SO₂

(440-520)S ppm
(17-19.9)S#/1000#

(52-520)S ppm
(2.0-20)S#/1000#

SO₃

6-24 ppm
(0.063-0.69)S
#/1000#

0-76 ppm
(0.063-2.9)S
#/1000#

NO

180-700 ppm

210 ppm
(f, tangential)
470 ppm
(f, horiz.)

310-915 ppm

330-915 ppm

NO₂

HC

0.4#/1000#

0-5#/1000#

PARTICULATE

0.025-0.060 gr/SCF

0.033 gr/SCF

0.005-0.205
gr/SCF

0.82-1.8#/1000#

1#/1000#

0.15-6.3
#/1000#

CYCLE &
TRANSIENTS

REMARKS

SOURCE

551

551

551

469

466 cited in 551

FUEL: OIL					
SIZE: LARGE					
LOAD (#/hr)	>1000 MW	>1000 MW	175 MW	>1000 BHP	
VELOCITY OR VOLUME					
TEMPERATURE (°F)					
O ₂ (%)					
CO ₂ (%)					
CO					
SO ₂					
SO ₃					
NO	500-700 ppm	100-900 ppm	310-915 ppm	275-600 ppm	*0.78#/10 ⁶ BTU (average for 554 samples) 14.2#/1000# (18,300 BTU/#)
NO ₂					
HC					
PARTICULATE					
CYCLE & TRANSIENTS					
REMARKS					* good
SOURCE	470 cited in 551	471	465 cited in 551	198 cited in 551	

FUEL: OIL					
SIZE: LARGE					
LOAD (#/hr)					
VELOCITY OR VOLUME					
TEMPERATURE (°F)					
O ₂ (%)					
CO ₂ (%)					
CO					
SO ₂	90%S+SO ₂ 1-5% SO ₂ ² +SO ₃	100%S+SO ₂ 1-2%S+SO ₂ *2200 ppm SO ₂	1-5%+SO ₃		
SO ₃					
NO	NO _x f(XS air) NO _x f(1oad)				160-699 ppm
NO ₂					
HC					
PARTICULATE	0.02-0.04 gr/SCF	0.14#/1000#			
CYCLE & TRANSIENTS					
REMARKS		* 4% S/oil			
SOURCE	551	cited in 551	471	465	467

FUEL: OIL		
SIZE: LARGE		
LOAD (#/hr)	5×10^8 BTU/hr	
VELOCITY OR VOLUME		
TEMPERATURE (°F)		
O ₂ (%)		
CO ₂ (%)		
CO		
SO ₂		
SO ₃		
NO		230#/hr
NO ₂		320-920 ppm
HC		
PARTICULATE		
CYCLE & TRANSIENTS		
REMARKS		
SOURCE	463	464

FUEL: OIL
SIZE: INTERMEDIATE

LOAD (#/hr)

<1000 BHP
Recommended

<1000 BHP
Usual Range

<1000 BHP
Extreme Range

VELOCITY OR
VOLUME

TEMPERATURE (°F)

O₂ (%)

CO₂ (%)

CO

SO₂

SO₃

NO

NO₂

HC

PARTICULATE

CYCLE &
TRANSIENTS

REMARKS

SOURCE

15 ppm
0.25#/1000#

(510)S ppm
(19.6)S#/1000#

5.25 ppm
0.25S#/1000#

320 ppm
9#/1000#

0-120 ppm
0-2#/1000#

(0-520)S ppm
(0-20)S#/1000#

(0-6.5)S ppm
(0.31)S#/1000#

0.140 ppm
0-4#/1000#

0-1100 ppm
0-194#/1000#

(365-520)S ppm
(14-20)S#/1000#

(0-6.8)S ppm
(0-3.4)S#/1000#

0-630 ppm
0-18#/1000#

47 ppm
0.33#/10⁶BTU

0.065-230#/hr

0.049 gr/SCF

1.5#/1000#

0.033-0.13
gr/SCF
1-4#/1000#

0-0.33 gr/SCF

0-10#/1000#

551

551

551

93

463

LOAD (#/hr)	<20x10 ⁶ BTU/hr	1100#steam/hr	60 HP	200 HP	350 HP
VELOCITY OR VOLUME					
TEMPERATURE (°F)					
O ₂ (%)			65% XS	210% XS	94% XS
CO ₂ (%)			0.01%	0.02	0
CO			355 ppm	11 ppm	17 ppm
SO ₂			1.6 ppm	5.6 ppm	0
SO ₃					
NO	usually not over 100 ppm	300 ppm	47 ppm	21 ppm	72 ppm
NO ₂		100% load 50% 25%			
HC					
PARTICULATE			0.069 gr/SCF	0.14 gr/SCF	0.014 gr/SCF
CYCLE & TRANSIENTS			1%S, #2	0.97%S, #2	0.42S, #2
REMARKS		464	461		
SOURCE	463				

FUEL: OIL
SIZE: INTERMEDIATE

LOAD (#/hr)	100 HP	200	245	120	125	245
VELOCITY OR VOLUME						
TEMPERATURE (°F)						
O ₂ (%)	290% XS	370% XS	115% XS	68% XS	180% XS	43% XS
CO ₂ (%)						
CO	0	0.002	0.002	0.003	0	0
SO ₂	98 ppm	neg.	102 ppm	414 ppm	264 ppm	397 ppm
SO ₃	1.4 ppm	0	0.5 ppm	4.7 ppm	3.2 ppm	0.4
NO } NO ₂ } ppm	36	55	33	368	128	387
HC						
PARTICULATE gr/SCF	0.071	0.10	0.041	0.074	0.11	0.064
CYCLE & TRANSIENTS						
REMARKS	0.71%S,#2	0.55%S,#2	0.21%S,#2	1.0%S,#6	1.78%S,#6	0.44%S,#6
SOURCE	461	461			461	

FUEL: OIL	425 HP	460 HP	500 HP	21x10 ⁶ BTU/hr	200 HP	225 HP	257 HP	350 HP
SIZE: INTERMEDIATE:								
LOAD (#/hr)								
VELOCITY OR VOLUME								
TEMPERATURE (°F)								
O ₂ (%)	110% XS	107% XS	92% XS.			486 av.		
CO ₂ (%)						2.7-10.3		
CO (%)	0.001	0	0			10.3%		
SO ₂ ppm	700	362	594			N-40 ppm		
SO ₃ ppm	6.7	2.2	3.6			160-997		
NO ppm							61-127 ppm	
NO ₂ ppm	275	199	256				9.8-37 ppm	
HC				0.31#/10 ⁶ BTU				
PARTICULATE gr/SCF	0.28	0.039	0.045					12.5#/1000 gal
CYCLE & TRANSIENTS								
REMARKS	0.06%S, #6	0.078%S, #6	1.39%S, #6					
SOURCE		461		459				

FUEL: OIL			
SIZE: SMALL			
LOAD (#/hr)	350,000 BTU/hr	1 gph	
VELOCITY OR VOLUME			
TEMPERATURE (°F)			
O ₂ (%)			5.5-12.8% (0-150% XS)
CO ₂ (%)			5.9-9.6%
CO			0.86-96.6 gm/Kg 10,000 ppm @ 0% XS Air extreme 1,000 ppm @ 25% XS (Best)
SO ₂			1.46-1.96 gm/Kg
SO ₃		negligible	<0.02 gm/Kg <0.05 ppm
NO			85-92% of NO _x
NO ₂		.065#/hr	1.08-2.41 gm/Kg 40-52 ppm, 46@ 25% XS air (equilib. should be 150-650 ppm)
HC			25 gm/Kg = 2700 ppm HC extreme 300 ppm @ 25% XS to zero @ 175% XS
PARTICULATE			0.04-33.40 gm/Kg
CYCLE & TRANSIENTS			On for 11.4 min Every 34 min.
REMARKS			0.098%, #2
SOURCE	463		512

FUEL: OIL				
SIZE: SMALL				
LOAD (#/hr)	0.17×10^6 BTU/hr	0.18×10^6	5000 K cal/hr	
VELOCITY OR VOLUME				
TEMPERATURE (°F)				
O ₂ (%)				
CO ₂ (%)				
CO			CO is high when soot high	2600 ppm on lighting 200-1000 after 10 min
SO ₂				
SO ₃			200-800 mg/m ³ STP 30 mg/m ³ @ max load 0-3% variation shown vs XS air	0.75-1.75% SO ₂ +SO ₃ about 20% of S in soot
NO				
NO ₂				
HC				
PARTICULATE	0.44×10^6 BTU	0.1×10^6 BTU		8.6 mg/m ³ +6.35 13 mg/m ³ +7.65
CYCLE & TRANSIENTS				
REMARKS			vaporizing burner	atomizing
SOURCE	459	459	55	55

FUEL: OIL	
SIZE: SMALL	
LOAD (#/hr)	0.66-2.5 gph
VELOCITY OR VOLUME	
TEMPERATURE (°F)	362-1025 682 average
O ₂ (%)	
CO ₂ (%)	
CO	N-1500 ppm
SO ₂	23.3-194 ppm
SO ₃	
NO	3.9-76 ppm
NO ₂	N-26.4
HC	
PARTICULATE	
CYCLE & TRANSIENTS	
REMARKS	
SOURCE	

FUEL:	GAS		
SIZE:	LARGE		
LOAD (#/hr)			
VELOCITY OR VOLUME			
TEMPERATURE (°F)			
O ₂ (%)			
CO ₂ (%)			
CO			
SO ₂			
SO ₃			
NO			
NO ₂		190-1350 ppm	180 ppm-1100 ppm
HC			
PARTICULATE			
CYCLE & TRANSIENTS		100#/hr @ 5x10 ⁸ BTU/hr	
REMARKS			
SOURCE		463	464 cited in 463

FUEL: GAS			
SIZE: INTERMEDIATE			
LOAD (#/hr)	$3 \times 10^5 - 5 \times 10^8$ BTU/hr	10^7 BTU/hr	9.3×10^6
VELOCITY OR VOLUME			
TEMPERATURE (°F)			
O ₂ (%)			
CO ₂ (%)			
CO			
SO ₂			
SO ₃			
NO			
NO ₂	8.47 ppm 0.06#/10 ⁶ BTU	90 ppm 0.16#/10 ⁶ BTU	0.14#/10 ⁶ BTU
HC			
PARTICULATE			
CYCLE & TRANSIENTS			
REMARKS			
SOURCE	198	462	459

APPENDIX 2

LITERATURE SEARCH

A comprehensive search of the literature was conducted to learn of all methodology which might be applicable to this program. This includes methods currently in use, those used in the past which seemed appropriate, and information from other areas which seemed relevant.

In order to perform this study we made a thorough search of the literature both past and present. Thus, we covered the journals, abstracts, indices and bibliographies shown in Tables 2-1 and 2-2. By this approach we feel we covered all journals in the western world and many others which might have any pertinence to this problem. To supplement this, we requested and obtained a literature search by APTIC on sampling and analytical methods for the pollutants of interest.

As articles of interest were uncovered by the literature research staff, the papers were studied by analytical chemists and significant information abstracted for further evaluation. As the study progressed, group discussions were held with chemists with relevant experience in order to both evaluate existing methods and seek fresh alternatives.

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TABLE A2-1
PRIMARY LITERATURE SOURCES UTILIZED IN THIS PROGRAM

Air Pollution Control Abstracts	1956-1969
Air Pollution Titles	Thru 1969
American Petroleum Institute Proceedings	1962-1969
Analytical Abstracts	1954-1969
Applied Science and Technology Index	1939-1969
Chemical Abstracts	1907-1968
Chemical Titles	Thru 1969
Engineering Index	1939-1969
Fuel Abstracts and Current Titles	1960-1969
SAE Progress in Technology Series	1961-1967

TABLE A2-2
BIBLIOGRAPHIES

Air Pollution Publications: A Selected Bibliography
(DHEW) 1963-1966

DDC Bibliography on Air and Water Pollution
(1968) AD 679210

Research into Sampling, Analysis and Monitoring of
Gaseous Pollutant Emissions from Stacks
Literature Searches I and II (Engineering
Found) 1963, 1965

Sulfur Oxides and Other Sulfur Compounds
A.G. Cooper, DHEW 1965

APPENDIX 3

DISCUSSION AND ADDITIONAL STUDIES OF THE BARIUM CHLORANILATE METHOD FOR SULFATE

A. DISCUSSION

1. Bertolacini and Barney (164) developed a method which consists of adding 0.3 g of barium chloranilate to a 50% ethanolic solution containing sulfate ion. The solution is buffered to pH 4 due to absorbance dependence on pH. Measurement is done colorimetrically at 530 nm.

a. Range is reported to be 2-400 ppm sulfate (2 ppm using 5 cm cells).

b. Accuracy and precision is given as approximately 1%.

c. Cationic interference is eliminated by use of an ion exchange column. Anion interference said to be negligible.

d. Time of mixing after addition of barium chloranilate was 15 minutes. Absorbance increased an additional 5% in 24 hours. Total time for analysis is 20 minutes.

2. Bertolacini and Barney (311) have done further work on the use of barium chloranilate in the determination of sulfate ion and found that acid chloranilate solutions have about 30 times greater absorption at 332 nm than at 530 nm. As in paper (1), solutions were put through cation exchange columns, buffered to pH 4 in 50% alcoholic solution and 0.2 g barium chloranilate added. Solution shaken for 15 minutes, then filtered. Filtrate absorbances were read at 332 nm in 1 cm cells against a reagent blank.

Preceding page blank

a. Range - Down to 0.06 ppm in 1 cm cell, upper limit not given.

b. Accuracy and Precision - Standard deviation of 0.2 ppm over a range of 0.98 to 3.86 ppm standards. (5-20% relative)

c. Interferences - Dish washing detergents. 2500 ppm nitrate ion produces an absorbance equivalent to 0.3 ppm sulfate. Sulfite does not interfere.

d. Time - About 30 minutes.

3. Carlson, Rosell and Vallejos (273) have made further modifications to the Bertolacini and Barney procedures by making use of solution equilibrium at varying pH's. They, therefore, add the buffer (a mixture of phosphoric acid and potassium dihydrogen phosphate) after filtering the chloranilate solution. Measurements were done at 530 nm. The calibration curve is non linear.

a. Range not reported.

b. Accuracy and Precision - Accuracy is within 3% of known amount.

c. Interferences - Removed by ion exchange column.

d. Time - Sample and barium chloranilate mixed for 1 hour. Total time is thus about 1 hour, 15 minutes.

4. Klipp and Barney (361) have modified the Bertolacini and Barney procedure by changing the buffer from potassium acid phthalate to a 0.02 M solution of sodium acetate-acetic acid. Buffer capacity has thus been increased to eliminate post filtration re-adjustment of pH.

a. Range - Sulfur in naphthas determined over range of 1-400 ppm 0-40 ppm calibration curve run at 330 nm, 40-400 ppm calibration curve run at 530 nm.

b. Accuracy and Precision - Standard deviation of about 3 ppm at 150 ppm sulfur level, 1 ppm at 25 ppm sulfur level. (2-4% relative)

c. Interferences - Removed by ion exchange.

d. Time - About 20 minutes (after oxidizing sulfur to sulfate).

5. A paper by Kanno et al (360) recommends a pH change from 4.0 to 5.2 to give more reliable results using the Bertolacini and Barney procedure.

6. Laxton and Jackson (153) automated the Bertolacini and Barney procedure. A silica wool probe filter was used to screen out cationic interferences. No buffer was used. The sample is collected in 80% isopropanol, and the sulfuric acid-isopropanol solution is passed through a 5-10 mm bed of barium chloranilate supported on a sintered glass filter. A second finer filter removes precipitated barium sulfate and fine particles of barium chloranilate. The filtered solution flows into a cell for measurement.

a. Range - Beer's Law plot up to 100 $\mu\text{g/ml}$ SO_3 has only slight curvature at lower end.

b. Color Development - 94% of absorbance resulting from 12 hour solution-reagent contact is achieved in the time needed for solution to reach the cell.

c. Interferences - Dissolved SO_2 at concentrations of 80 $\mu\text{g/ml}$ caused less than 0.1% change in solution color.

d. Time - About 5 minutes.

B. ADDITIONAL LABORATORY STUDIES

1. Introduction

In Section 5.5.4.2 of this report, the principal laboratory investigations of the barium chloranilate system at the adopted pH 5.6 were described. In this section we report on additional work conducted on this method, principally of a preliminary or auxiliary nature.

A study was conducted to evaluate some variations in the barium chloranilate colorimetric method for sulfate, specifically buffering systems given in the literature (164,311,153,271,273) to determine:

- a. adherence to Beer's law
- b. sensitivity
- c. time and amount of mixing needed prior to absorbance measurement

Work on the acetate-acetic acid buffer system (pH 4.6) showed adherence to Beer's law up to at least 250 $\mu\text{g SO}_4^{--}/\text{ml}$ of solution. The sensitivity was 0.002 absorbance units per μg . Initial measurements revealed that the curve deviates from Beer's law between 250 $\mu\text{g}/\text{ml}$ and 500 $\mu\text{g}/\text{ml}$ concentration. At 0.002 absorbance units/ $\mu\text{g SO}_4^{--}/\text{ml}$ solution, the method is sensitive enough to determine 8 mg/M^3 of SO_3 in flue gas (assuming no interferences).

Preliminary work on the phosphate-phosphoric acid buffer system (pH 1.8) indicated that the system may have greater sensitivity than the acetate-acetic acid system, but may not be as useful since the operable range would be limited. A single run on the non-buffered system using 80% isopropanol solvent indicated a decrease in sensitivity compared to the acetate-acetic acid system.

2. pH Dependence

Three of the literature methods were run for comparison purposes. The methods were those conducted at pH 1.8 (273), 4.0 (164), and 4.6 (361). Results indicate little difference between the pH 4.0 and 4.6

systems. The pH 1.8 system appears to be much more sensitive than either the 4.0 or the 4.6 system, e.g., 250 $\mu\text{g SO}_4^{=}/\text{ml}$ gives the following absorbancies vs water at 530 nm after 15 minutes mixing.

<u>pH</u>	<u>Absorbance Corrected for Blank</u>	<u>Absorbance of Blank</u>
1.8	1.64	0.107
4.0	0.520	0.013
4.6	0.500	0.013

Since the applicable dynamic concentration range would be more limited with the pH 1.8 system due to the steepness of the slope (0.006 absorbance units/ μg), we have ruled out the pH 1.8 system.

A comparison of data for the pH 4.0 and 4.6 systems is as follows: Solutions were shaken (hand shaking 10 shakes every 2 minutes) for 15 minutes followed by five minutes centrifuging to separated unreacted barium chloranilate and precipitated barium sulfate from the centrifugate. (An International Clinical Model centrifuge was used - 6-place head, 15 ml tubes at highest speed setting.) The absorbance was measured vs a water blank on a Beckman DU spectrophotometer in 1 cm cells at 530 nm. All water used for solution preparation was percolated through a bed of Amberlite MB-3 ion exchange resin to remove sulfate ion from the water. The calibration data obtained for both pH ranges are given below:

<u>Concentration ($\mu\text{g}/\text{ml}$)</u>	<u>Absorbance</u>	
	<u>pH 4.0</u>	<u>pH 4.6</u>
0	0.013	0.013
50	0.127	0.116
125	0.281	0.267
250	0.533	0.513
500	0.778	0.752

3. Removal of Precipitate Prior to Color Readout

Solutions were initially filtered through Whatman No. 42 paper after reaction with the barium chloranilate. However, this is

quite slow and the possibility of concentration changes while filtering suggested we find an alternative. A comparison of filtration vs centrifugation on an International Clinical Model showed a difference of 0.005 absorbance units between filtered and centrifuged solutions at the 0.500 absorbance level (or a 1% difference on the samples measured). Since centrifugation was faster and gave comparable results, we have since followed the practice of centrifuging rather than filtering solutions.

APPENDIX 4

SAMPLING SYSTEM FOR SO_x AND NO_x

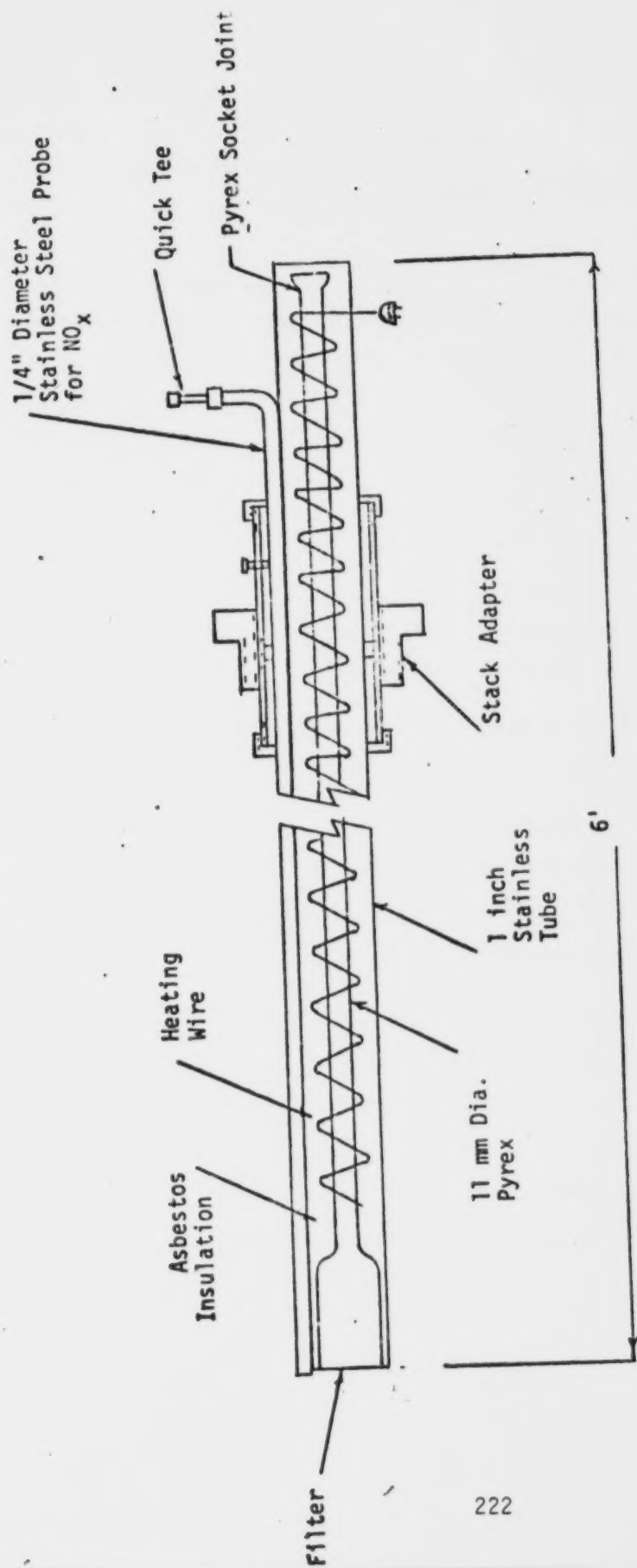
Equipment for sampling SO_x (and NO_x) gases from combustion flue gases has been designed. The objectives of the design were first to provide high precision and secondly to make the equipment convenient to transport, install and operate at field locations. The system is comprised of the following three modules:

1. dual probe module
2. SO_x and NO_x collection module
3. control module

The above modules constitute a complete system for sampling for SO_3 , SO_2 and NO_x in the flue gas.

Probe Module - A schematic of the probe module is shown in Figure A4-1. The features of this module are:

1. dual probes, a 1/4 inch diameter stainless steel probe for NO_x mechanically coupled to 11 mm pyrex probe for SO_x .
2. pyrex probe electrically heated to prevent condensation of SO_3 in the sampling line.
3. stack adapter assembly that allows various probe insertion depths.
4. filter in the probe to remove particulates from the SO_x sample gas.
5. quick attachment tees for NO_x grab samplers.
6. pyrex socket joint for connection to collector module.



PROBE MODULE

Figure A4-1

SO_x Collector Module - The collector module depicted in Figure A4-2 has two principal parts, the SO₃ condenser and the SO₂ impinger train. The SO₃ condenser is a pyrex coil with a glass frit filter attached to the downstream end. This assembly with an electric heating coil and thermostat is encased in a two inch diameter copper water jacket. The thermostat will maintain the water temperature at 140°F. The upstream end of the condenser assembly terminates in a pyrex ball joint which mates with the socket joint on the probe module. The downstream end of the condenser assembly also terminates in a pyrex ball joint which mates with a socket joint on the SO₂ impinger train assembly.

The SO₂ impinger train assembly consists of two midget impingers modified with ball and socket joint connectors.

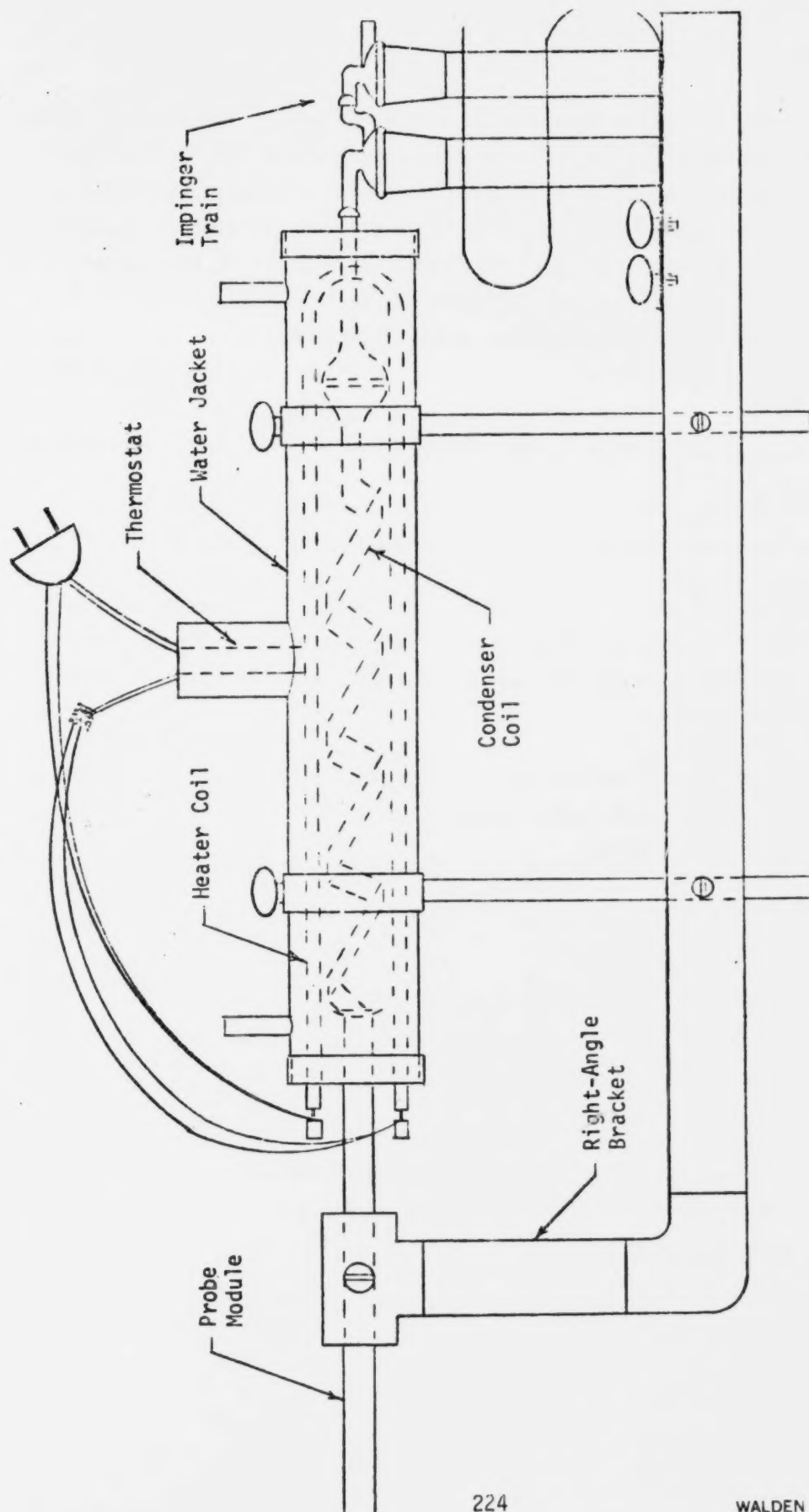
The SO_x collection module is mechanically connected to and supported by the probe through a right-angle bracket. The SO₃ condenser assembly and SO₂ impinger train are separately attached to the right-angle bracket.

The SO_x collection module is pneumatically connected to the control module through rubber vacuum hose.

Control Module - The control module is shown in Figure A4-3. The principal components of this module are:

1. vacuum pump
2. critical orifice meter
3. SO_x probe heater power supply
4. power control panel

The vacuum pump is a Gast Model 1531. This pump is capable of achieving a static vacuum of 26" Hg, and maintaining a pressure drop sufficient for critical flow across a 3ℓ/min critical orifice when connected to the sampling system.



COLLECTOR MODULE

Figure A4-2

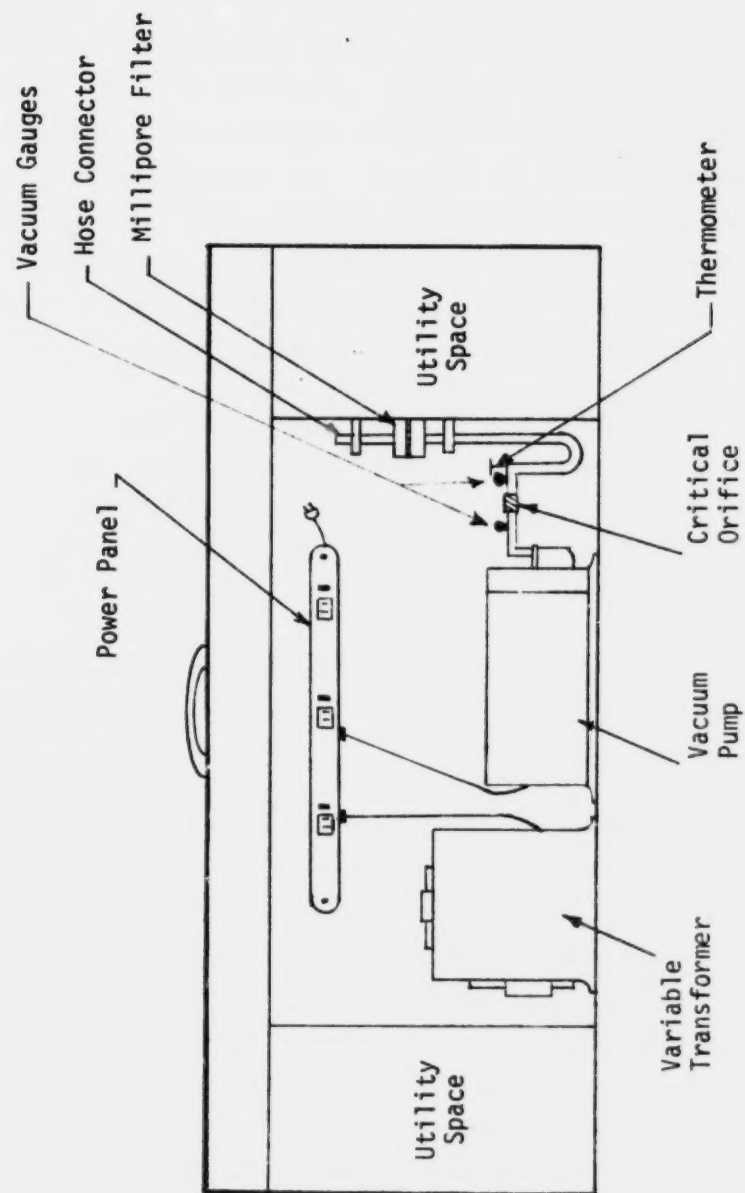


Figure A4-3. Control Module (front panel not shown).

The critical orifice meters (Millipore) are available as stock items in the sampling rates of interest for this system (0.5, 1.0 and 3.0 /min). Vacuum gauges are provided upstream and downstream of the critical orifice in order to monitor the critical flow condition, i.e., $\Delta P > 7.6''$ Hg. A thermometer is placed in the sampling line just upstream of the critical orifice. The temperature from this thermometer and the pressure from the upstream pressure gauge may be used to convert the sample gas volume to a volume at other conditions. A Millipore filter is placed in the sample line just upstream of the critical orifice to protect the orifice against plugging.

A variable transformer provides the heater power supply for the SO_x probe. During test of the sampling systems, this transformer is adjusted to maintain the SO_x probe temperature above the condensation temperature of SO_3 . The control will be locked to prevent misadjustment in field operations.

The pump motor, the variable transformer and the power line to the SO_3 condenser are plugged into the control panel and controlled by the separate switches.

System Operation - The probe module is fitted to a stack or flue and the sampling lines connected as previously described. Power cords are connected between the SO_x probe heater and the variable transformer and between the SO_3 condenser and the power control panel. Water is added to the SO_3 condenser jacket and peroxide solution added to the SO_2 impingers. The probe heater and SO_3 condenser are switched on at the control panel and time allowed for them to come to operating temperature. Then, the pump is started from the control panel switch and the time recorded. During the sampling period, the operator checks ΔP across the critical orifice and records the pressure and temperature values. At this time, he may collect NO_x grab samples in an evacuated 2ℓ flask through the NO_x probe. At the end of the sampling period, the

pump is switched off and the time recorded. The SO_x sample is calculated from the time interval and the flow rate value of the critical orifice. The SO_3 collected in the condenser and the SO_2 collected in the impinger are transferred to sample bottles and the system may be recycled for replicate samples.

APPENDIX 5

LABORATORY DILUTION SYSTEMS

A. SO_2

A simple dilution system for producing high concentrations (>200 ppm) of SO_2 , NO (and NO_2) was constructed (Figure A5-1).

The dilution system contains a pump for delivery of dilution air; calibrated flow meters for air, SO_2 , NO and NO_2 ; and a 5-liter mixing vessel.

All tubing used in the original equipment was either glass or viton. Air flow through the system is 10 to 15 liters/min. After mixing, a small fraction of the total (0.5 to 5 liters/min) is withdrawn from the exhaust.

A series of blank runs following high concentration SO_2 absorption efficiency tests showed significant SO_2 desorption was occurring. Since the dilution system was constructed of glass and viton tubing, we concluded that significant desorption of SO_2 from viton was occurring. The viton tubing (Figure A5-2) in the collection system was replaced with glass tubing. This eliminated the SO_2 background. All test results were obtained with this system.

B. SO_3 DILUTION SYSTEM

The SO_3 dilution system constructed is considerably different from the SO_2 dilution system because of the high reactivity and low volatility of SO_3 and the addition of water vapor injection to simulate a combustion effluent.

The system constructed was all glass (Figure A5-3). Dry air passes through a flow meter into a thermostated flask containing solid SO_3^* (vapor pressure at room temperature is about 0.1 atm). The dry

*Obtained as stabilized liquid (Sulfan) from Allied Chemical Corp.

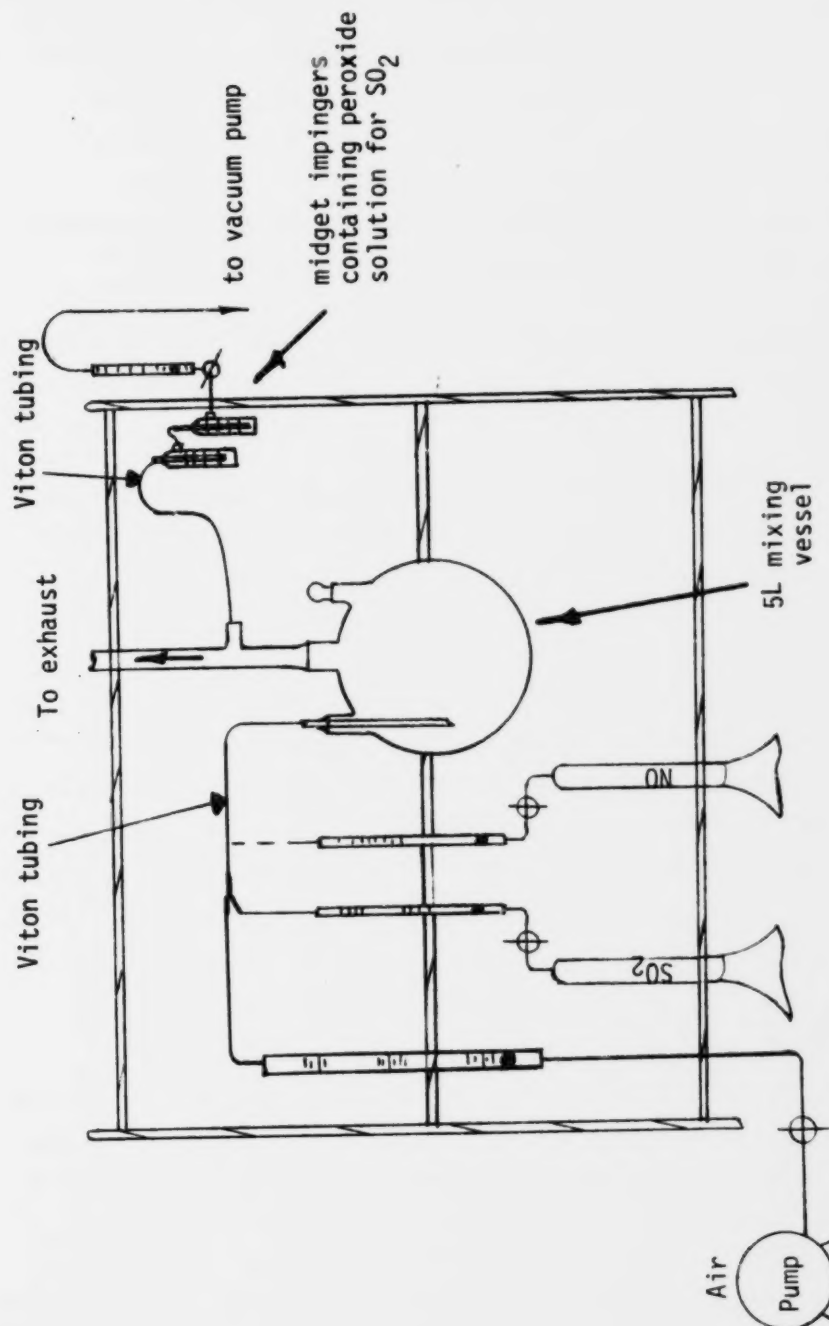


Figure A5-1. Simple dilution system for high concentrations of SO_2 and NO

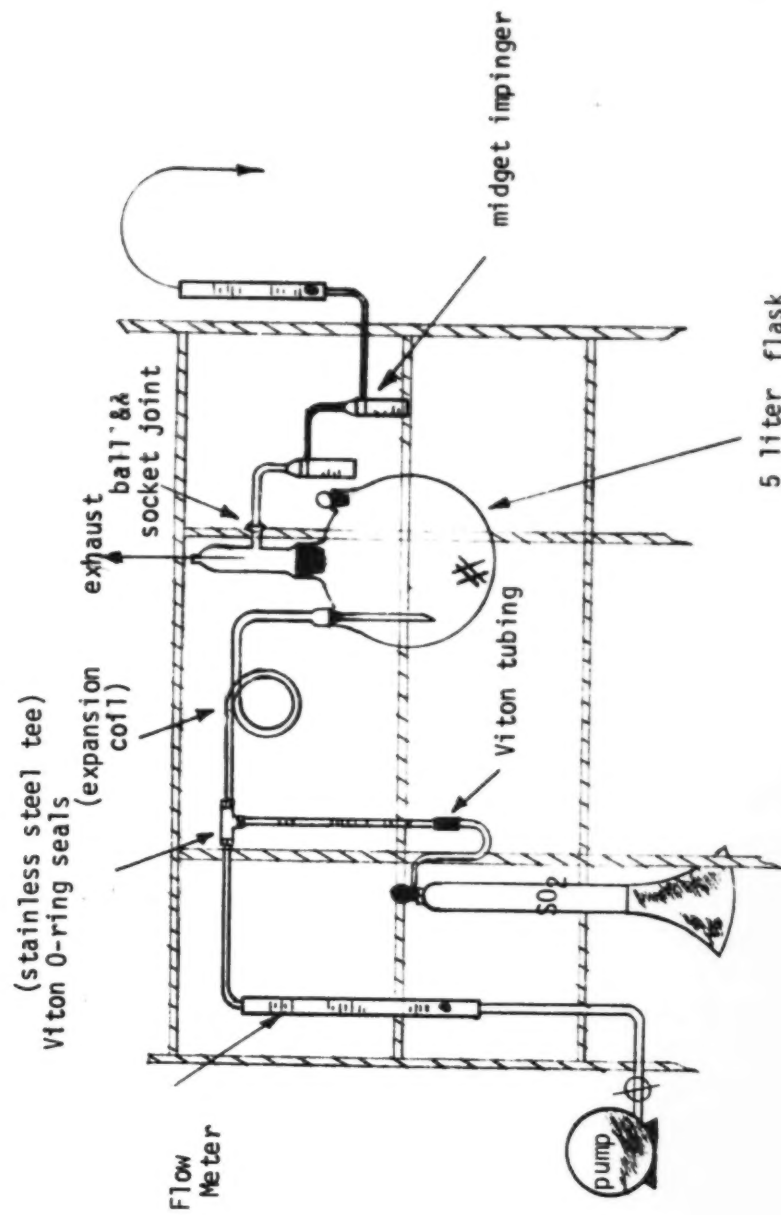


Figure A5-2. Dilution System.

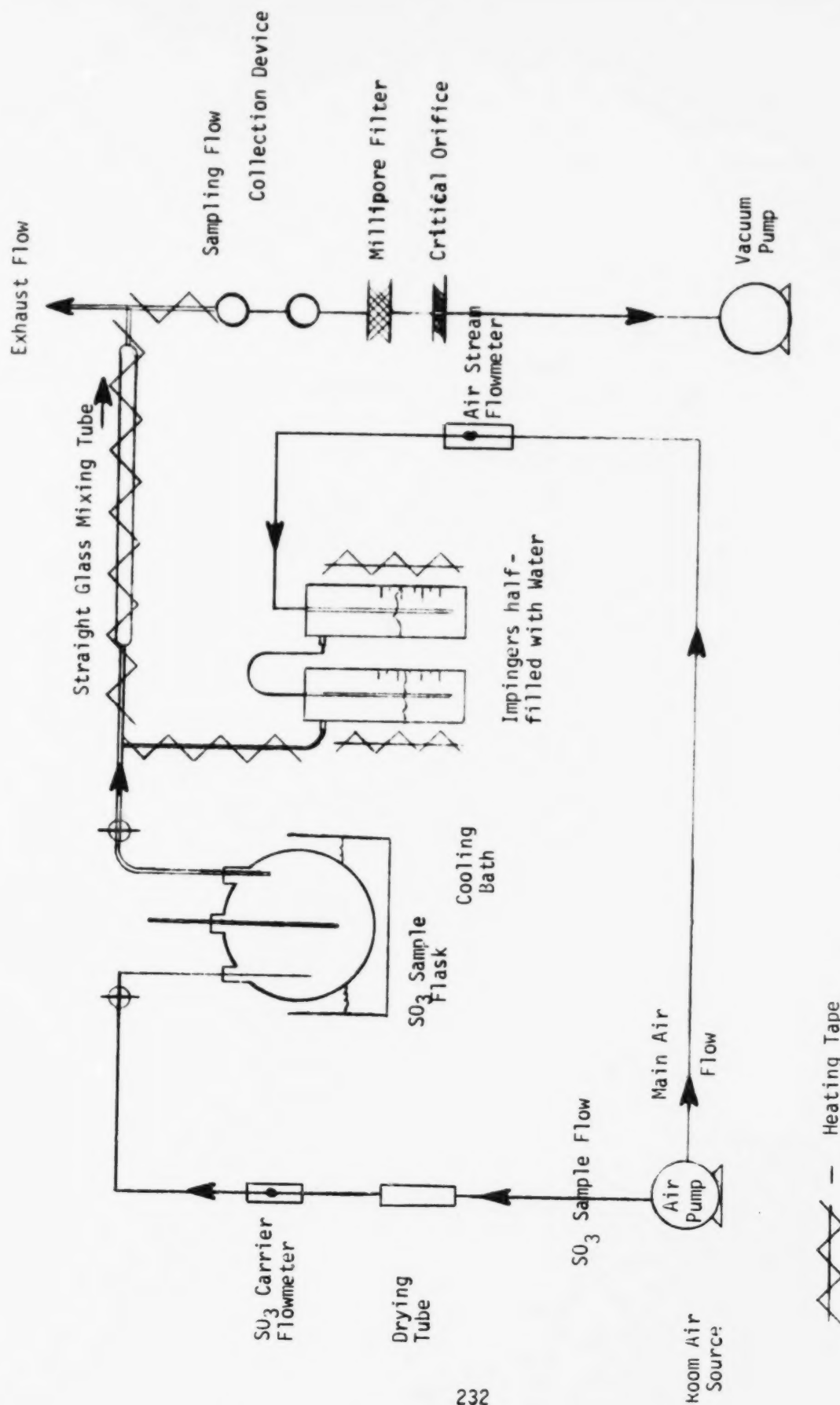


Figure A5-3. SO₃ Delivery System

SO_3 air mixture leaving the flask is mixed downstream with moist air saturated with water at a known temperature. The entire flow system, with the exception of the SO_3 vessel, is electrically heated to prevent condensation of H_2SO_4 or H_2O .

Since both the SO_3 and moist air supplies are metered prior to treatment, the ambient temperature calibration factors may be used to establish the flow rates. SO_3 concentrations may be established by control of temperature and/or dilution ratios. The water vapor concentration of the output stream was determined using weighed CaCl_2 absorption tubes and/or impingers cooled in a salt-ice bath. The moisture content was in the range 8 to 12% (in good agreement with the desired values for a simulated combustion effluent).

The delivery system for SO_3 was originally constructed with a spiral mixing section. This was replaced by a straight run of electrically heated glass tubing to obtain improved heat transfer and eliminate a severe condensation problem.

Difficulties in obtaining low concentrations (50 to 150 ppm SO_3) were solved by crystallizing the (α) solid phase from the stabilized liquid (Sulfan). This reduced the vapor pressure by an order of magnitude. The SO_3 concentration is, however, still not well-controlled in this apparatus. Even with the reservoir thermostated, run to run variations by a factor of 10 were not uncommon.

APPENDIX 6

BIBLIOGRAPHY FOR HYDROGEN SULFIDE

At the initial outset of our work, we were required to perform a literature search on existing analytical methods applicable to the determination of hydrogen sulfide (H_2S) in combustion effluents. However, this task was changed early in the program in favor of emphasis on carbon monoxide.

This report is intended to cover the limited amount of work that was spent on H_2S . Thus, it is not intended in any sense to be complete - either with regards to methodology or the bibliography.

The methodology for H_2S can be grouped into a number of categories: colorimetric, titrimetric, and turbidimetric. H_2S undergoes a variety of chemical reactions (oxidation-reduction, acid-base, complexation, etc.) and all of these have been employed in developing the methods currently available. Based on our brief exposure, it appears that a number of these methods have sufficient sensitivity and precision for use in analysis of fossil fuel combustion products. However, none are truly specific for H_2S so that accuracy would be questionable.

On the following pages are presented the literature which was found for the determination of H_2S . It is divided into sub-categories by method as well as being presented at the end as a bibliography by author.

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REVIEW, EVALUATION AND DISCUSSION PAPERS

The following papers provide reviews of the procedures for H₂S.

- RP1 Risenfield, F.C. and Orbach, H.K. "Methods for Determining Hydrogen Sulfide in Gases". Petroleum Engineer, 25(6) (1953) C32-8. (CA 49: 12197, 1955).
- RP2 Brychta, Miroslav and Štrobl, Jiř. "Hydrogen Sulfide Determination in Illuminating Gas". Paliva, 32 (1952)p. 113-116. (CA 50: 8173, 1956).
- RP3 Jacobs, M.B. The Chemical Analysis of Air Pollutants. p. 182-194. Interscience Publishers, Inc. N.Y. 1960.
- RP4 Smith, A.F., Jenkins, D.G. and Cunningworth, D.E. "Measurement of Trace Quantities of Hydrogen Sulphide in Industrial Atmospheres". Journal of Applied Chemistry, 11 (Sept. 1961) p. 317-29.
- RP5 Lahmann, Erdwin. "Measurement of Gaseous Sulfur Compounds in the Atmosphere". Erdoel und Kohle, 18(10) (1965) p. 796-800. (CA 64: 1966).
- RP6 Jensen, George A., Adams, Donald F. and Stern, Harry. "Absorption of H₂S and Methyl Mercaptan from Dilute Gas Mixtures". Journal of Air Pollution Control Association, 16(5) (1966) p. 248-53. (CA 65: 1966).
- RP7 Bamesberger, W.L. and Adams, D.F. "Improvements in the Collection of Hydrogen Sulfide in Cadmium Hydroxide Suspension". Environmental Science and Technology, 3(3) (March 1969) p. 258-61.

PROCEDURES BASED ON METHYLENE BLUE REACTION

One of the more sensitive and selective procedures for H_2S is based on trapping in zinc acetate solution and reaction of the zinc sulfide with ferric ion, and p-amino dimethyl aniline in acid solution. The resultant product is blue and can be measured spectrophotometrically. Of the references listed below, the paper by Gustafsson (MB5) provides a good discussion of the color reaction, while the others are oriented towards a specific application.

- MB1 Kosior, K.E.A. "Determination of Hydrogen Sulfide in Natural Gas". Canadian Chemistry and Process Industry, 32 (1948) p. 925-6, 929. (CA 43: 835, 1949).
- MB2 Fogo, James K. and Popowsky, Milton. "Spectrophotometric Determination of Hydrogen Sulfide-Methylene Blue Method". Analytical Chemistry, 21 (1949) p. 732-4. (CA 43: 7375, 1949).
- MB3 Sands, A.E., Grafius, M.A., Wainwright, H.W., and Wilson, M.W. "The Determination of Low Concentrations of Hydrogen Sulfide in Gas by the Methylene Blue Method." U.S. Bureau of Mines, Report of Investigations, no. 4547 (1949) 19 pp. (CA 44: 307e, 1950).
- MB4 Jacobs, Morris B., Braverman, M.M., and Hochheiser, Seymour. "Ultramicro-determination of Sulfides in Air". Analytical Chemistry, 29 (1957) p. 1349-51.
- MB5 Gustafsson, Lilly. "Determination of Ultramicro Amounts of Sulphate as Methylene Blue. I. The Colour Reaction". Talanta, 4 (1960) p.227-35.
- MB6 Choudens, C. de. "Quantitative Spectrophotometric Analysis for Sulphur Dioxide and Hydrogen Sulphide in Gaseous Effluents from Recovery Units of a Sulphate-Pulp Mill". Revue Association techq. Industrie Papetiere, 22(2) (1968) p. 113-121. (Ca 17: 1216, Aug. 1969).

REACTIONS WITH IODINE

As a reducing agent, H_2S is a natural for determination with an oxidant. Iodine has been used for this purpose for a long time. The major variations in methods based on determination with iodine are in how the H_2S is collected and prepared for titration (or reaction) with I_2 . Some employ a metal ion and then react with I_2 (I1, I7, I9, I11, I13, also I14), while others use I_2 as the absorbent (I3, I6, I8, I10) and back titrate with thiosulfate. The various references uncovered on the use of iodine are:

- I1 Zhdanov, V.V. "Rapid Methods for Determination of Hydrogen Sulfide in Coke-Oven Gas". Zavodskaya Laboratoriya Zhurnal, 6 (1937) p. 1448-51. (CA 32: 2323, 1938).
- I2 Cherepennikov, A.A. "Hydrogen Sulfide, Carbon Dioxide and Sulfur Contents of Natural Gas from the Bashneft Oil Wells". Neftyanoe Khozyaistvo, 2 (1937) p. 68-9. (CA 32: 4311₄, 1938).
- I3 Krafft, Hans. "The Chemical Laboratory in the Service of Safety in Mining". Montan. Rundschau, 31(20) (1939) p. 561-7. (CA 34: 5958₉, 1940).
- I4 Payer, Theo and Lehrenkrauss, Adolf. "Determination of Hydrogen Sulfide and Hydrocyanic Acid in Manufactured Gas". Gas und Wasserfach, 82 (1939) p.713-15. (CA 34: 609₆, 1940).
- I5 Strada, Mario, and Macri, Antonio. "Rapid Method for Determining Hydrogen Sulfide in Technical Gas Mixtures". Annali di Chimica Applicata, 29 (1939) p. 64-8. (CA 33: 8524₆, 1939).
- I6 Wilson, Stuart H. "The Analysis of Hot-Spring Gases". New Zealand Journal of Science and Technology, 20B (1939) p. 233-48. (CA 33: 6745₈, 1939).
- I7 Shaw, Joseph A. "Rapid Determination of Hydrogen Sulfide and Mercaptan Sulfur in Gases and in Aqueous Solutions". Industrial and Engineering Chemistry, Analytical Edition, 12 (1940) p. 668-71. (CA 35: 538, 1941).
- I8 Kraft, Janos. "The Chemical Laboratory as an Aid to Mine Safety". Banyaszati es Kohaszati Lapok, 75 (1942) p. 113-17. (CA 37:4153₈,1943).
- I9 Anon. "Test Procedure for Determining H_2S and Mercaptan Content of Natural Gas". American Gas Journal, 162(6) (1945) p. 47,60. (CA 39: 3413₆, 1945).
- I10 Kitano, Yasushi and Takakuwa, Hidematsu. "Determination of Hydrogen Sulfide and Sulfur Dioxide in Air. I. Errors in Iodometry". Japan Analyst, 3 (1954) p.7-10. (CA 48: 6913_e, 1954).

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- I11 Wickert, K. "The Determination of SO_2 , SO_3 , and H_2S in Flue Gases". Brennstoff-Warme-Kraft, 12 (1960) p. 449-51. (CA 55: 1961).
- I12 Cave, G.C.B. "The Collection and Analysis of Odorous Gases from Kraft Pulp Mills. I. Theoretical Considerations". Tappi, 46(1) (1963) p. 1-5. (CA 59: 8967, 1963).
- I13 Shul'gina, E., Arutyunova, A.Kh., Blyumshtein, A.E. "Determination of H_2S in Gases". Neftepererabotka i Neftekhimiya, Nauchn.-Tekn.Sb., 3 (1964) p. 26-9. (CA 61: 1964).
- I14 _____. "Separation and Determination of Mercaptans, Hydrogen Sulfide, Organic Sulfides, and Organic Disulfides, and Organic Disulfides in an Air Stream". Bay Area Air Pollution Control District, San Francisco, California, Method M-1.

INDICATOR TUBES

A variety of Approaches have been taken to develop indicator tubes for H_2S . These include: a paper impregnated with potassium hydroxide, potassium zincate and glycerol (IT9); lead acetate tiles (IT7); lead acetate paper (IT1, IT2, IT10, IT12); carriers impregnated with copper salts (IT4, IT5); silver cyanide (IT6); bismuth nitrate (IT11); lead acetate (IT14); metallic silver fibers (IT15). References found are:

- IT1 Eymanu, Constanz. "Determination of Hydrogen Sulfide and Hydrocyanic Acid in Gases". Gas und Wasserfach, 81 (1938) p. 484-8. (CA 32: 8112, 1938).
- IT2 Sliva, Vitezslav. "The Determination of Hydrogen Sulfide in Illuminating Gas". Plyn Voda a Zdravotni Technika, 18 (1938) p. 49-51. (CA 34: 42552, 1940).
- IT3 Littlefield, John B. "Determination of Constituents Such as Hydrogen Sulfide in Gaseous Atmospheres". (to Mine Safety Appliances Co.) U.S. 2,174,349. Sept. 26. (CA 34: 6926, 1940).
- IT4 Smith, Bengt. "Quantitative Analysis of Mixtures of Hydrogen Sulfide and Sulfur Dioxide". Transactions of Chalmers University of Technology, Gothenburg, no. 150 (1954) 19pp. (CA 49: 80411, 1955).
- IT5 Heuschkel, G. "Analysis of Gases Containing Hydrogen Sulphide and Sulphur Dioxide by Means of Indicator Tubes". Erdöl und Kohle, 14(6) (1961) p. 467-68. (AA 9: June 1962).
- IT6 Schumann, H., Lovenstrin, K., Blaschke, H. of VEB Chemiewerk Coswig. "Method and Device for the Determination of Hydrogen Sulphide in Gases". British Patent 1,047,700; date appl. 2/9/63. (AA 14: 5842, Sept. 1967).
- IT7 Gilardi, Edward F. and Manganelli, Raymond M. "A Laboratory Study of a Lead Acetate-Tile Method for the Quantitative Measurement of Low Concentrations of Hydrogen Sulfide". Journal of the Air Pollution Control Association, 13(7) (1963) p. 305-9.
- IT8 Vol'berg, N.Sh. and Gershevik, E.I. "Use of Solid Adsorbents in Industrial Sanitation Chemistry". Materialy k Nauchn. Sessii Posvyashch. 40-letiyu Gos. Nauchn.-Issled. Inst. Gigieny Truda i Profzabolevanii, Leningrad, Sb., 1964, 56. (CA 64: 1966).
- IT9 Huygen, C. "The Sampling of Hydrogen Sulfide in Air with Impregnated Filter Paper". Analytica Chimica Acta, 30(6) (1964) p. 556-564.

INDICATOR TUBES (CONTINUED)

- IT10 High, M.D. and Horstman, S.W. "Field Experience in Measuring Hydrogen Sulfide". American Industrial Hygiene Association Journal, 26(4) (July-August 1965).
- IT11 Sinkevish, O.V. and Noshchenko, A.E. "Determination of the Hydrogen Sulfide Content of the Air". USSR 174,002 (Cl.G 01n) Aug. 6, 1965. (CA 64: 1966).
- IT12 Leidnitz, Kurt. "Determination of Hydrogen Sulfide in Coke-oven Gas". Gas und Wasserfach, 106 (1965) p. 1204-6. (CA 66: 1967).
- IT13 Grosskopf, Karl. "Tube Method in the Analytical Laboratory". Fortschr. Chem. Forsch, 5(3) (1966) p. 530-67. (CA 65: 1966). (A review.)
- IT14 Ryashentseva, M.A. and Afanas'eva, Yu.A. "Adsorption-Chemical Determination of Hydrogen Sulfide and Sulfur Dioxide in Gas Mixtures". Khim Tekhnol. Topl. Masel, 12(3) (1967) p. 61-3. (CA 67: 1967).
- IT15 Falgout, D.A. and Harding, C.I. "Determination of H₂S Exposure by Dynamic Sampling with Metallic Silver Filters". Journal of the Air Pollution Control Association, 18(1) (1968) p. 15-20.

TURBIDIMETRIC METHODS

Trace quantities of H_2S can be estimated from the amount of precipitate formed after reaction with a metal ion. Copper (TM1), cadmium (TM2, TM3, TM5), bismuth (TM3), and arsenic (TM4) have been used for this purpose. The turbidity can be estimated visually or via use of a spectrophotometer. References found to this approach were:

- TM1 Kastner, E.P. "The Photocolorimetric Determination of Hydrogen Sulfide in the Air". Journal of Applied Chemistry, 12 (1939) p. 1097-1103. (CA 34: 3203, 1940).
- TM2 Bergström, H. and Trobech, K.G. "Investigations of Black Liquor". Svensk Papperstidning, 42 (1939) p. 554-7. (CA 34: 1171, 1940).
- TM3 Field, E. and Oldach, C.S. "Determination of Hydrogen Sulfide in Gases". Industrial and Engineering Chemistry, Analytical Edition, 18 (1946) p. 665-7. (CA 41: 54, 1947).
- TM4 Ethrington, C.G., Warren, H., and Marsden, F.C. "Colorimetric Determination of Small Amounts of Hydrogen Sulfide in Effluent Gases by Means of the Spekker Absorptiometer". Analyst, 75 (1950) p. 209-11. (CA 44: 6345g, 1950).
- TM5 Lahmann, Erdwin, and Prescher, Karl E. "Intermittent Hydrogen Sulfide Determination in the Atmosphere". Staub, 25(12) (1965) p. 527-8. (CA 64: 1966).

MISCELLANEOUS METHODS WITH A TITRATION READ OUT

In addition to those based on an iodine titration, a number of other methods have been developed with a titration read-out. Some are based on oxidation - ceric (TR1), permanganate (TR2). Others depend on reaction of H_2S with a metal ion and determination of the excess metal - mercury (TR5), cadmium (TR8, TR10) and zinc (TR9, TR10). A few utilize direct titration and a potentiometric end-point (TR3, TR6), another conductometric titration after collection in hydroxide (TR7), while another depends on catalysis for selectivity (TR4). The total list of references in this general category is:

- TR1 Lilly, R.M. and Chesnutt, N.P. "Determining Hydrogen Sulfide Content of Gas in the Field". Oil and Gas Journal, 36(14) (1937) p.52,55,58,70. (CA 31: 8885, 1937).
- TR2 Seuthe, Ad. "Determination of Hydrogen Sulfide in Coke-Oven Gas". Chemiker-Zeitung/Chemische Apparatur, 65 (1941) p. 59. (CA 35: 3416, 1941).
- TR3 Felicetta, V.F., Peniston, Q.P., and McCarthy, J.L. "Determination of Hydrogen Sulfide, Methyl Mercaptan, Dimethyl Sulfide, and Disulfide in Kraft Mill Process Streams". Canadian Pulp and Paper Industry, 5(12) (1952) p.16,18,20,22,24,26-7,30,41. (CA 47: 5115, 1953).
- TR4 Gershovich, E.E. "Catalytic Reactions in Industrial Sanitary Chemistry". Trudy Nauchnoi Sessii Leningradskogo Nauchno - Issledovatel'skogo Instituta Gigieny Truda i Profzabolevanii, 1958, p.153-8. (pub.1959). (CA 57: 1962).
- TR5 Hoffmann, E. "Mercurimetry in the Microquantitative Analysis of Iodides, Cyanides, and Sulfides in Solution and Hydrocyanic Acid and Hydrogen Sulfide in Gases". Zeitschrift fuer Analytische Chemie, 169 (1959) p. 258-63. (CA 54: 1960).
- TR6 Tamele, M.W., Irvine, V.C., and Ryland, L.B. "Potentiometric Determination of Sulfide Ions and the Behavior of Silver Electrodes at Extreme Dilution". Analytical Chemistry, 32 (1960) p. 1002-7.
- TR7 Oehme, F. "High-frequency Titrimetric Determination of Hydrogen Sulphide and Thiols in Technical Gases after Absorption in Alkaline Solution". Erdöl und Kohle, 13 (1960) p. 394-96. (AA 8: 1961).
- TR8 Baranenko, S.E. and Krivosheeva, V.I. "Trilonometric Determination of Hydrogen Sulfide in Natural, Accessory, and other Gases". Voprosy Razvitiya Gazovoi Promyshlennosti Ukrainskoi SSR, Kiev.Sb., (1963)p.300-3. (CA 61: 1964).
- TR9 Balabanoff, L. and Soto, L. "Rapid Determination of Hydrogen Sulfide with EDTA". Chimie Analytique, 46 (1964) p. 90-92. (AA 12: 1965).
- TR10 Zugrăvescu, P.G. and Zugrăvescu, M.A. "Determination of Trace Impurities (Acetylene, Phosphine, Arsine, Hydrogen Sulfide and Carbon Dioxide) in Gases". Revista de Chimie, 17(11) (1966) p. 704-5. (AA 15: Feb. 1968).

MISCELLANEOUS COLOR REACTIONS

Many different reactions have been employed to H_2S which end up with a color read-out. Some of these are based on the well known starch-iodine color (CR1), Lauth's violet (CR6), nitroprusside (CR7), and molybdenum blue (CR8, CR9). The complete bibliography found for this section was:

- CR1 Blohm, Clyde L., and Riesenfeld, Fred C. "Simultaneous Determination of Hydrogen Sulfide and Carbon Dioxide in a Continuous Gas Stream". Industrial and Engineering Chemistry, Analytical Edition, 18 (1946) p. 373-6. (CA 40: 4315g, 1946).
- CR2 Taramasso, M. and Piccinini, A. "Determination of Hydrogen Sulfide in Light Petroleum Gases". Rivista dei Combustibili, 9 (1955) p.933-9. (CA 50: 9724, 1956).
- CR3 Maksimov, V.F. "Volatile Sulfur Compounds in a Kraft Pulp Mill". Trudy Leningradskogo Tekhnologicheskogo Instituta imeni Lensoвета, 5 (1958) p. 19-22. (CA 56: 1962).
- CR4 Chetkowaka, M., Gallus-Olender, J., and Strzeszewska, I. "Continuous Determination of Hydrogen Sulfide in Air". Chemik, 14 (1961) p. 384-6. (CA 56: 1962).
- CR5 Gavrillets, E.S. and Demchuk, M.V. "Determination of CO_2 , NH_3 , and H_2S in the Air of Living Quarters". Naukovi Pratsi, L'vivskii Zooveterinarnii Institut, 11 (1961) p. 89-96. (CA 59: 12076, 1963).
- CR6 Murray, F.E. and Raynor, H.B. "A Procedure for Sampling and Analysis for Hydrogen Sulfide in Kraft Mill Stack Gases". Tappi, 44(3) (March 1961) p. 219-21.
- CR7 Mokhov, L.A. and Matveeva, S.A. "Colorimetric Determination of Hydrogen Sulfide in Air". Laboratornoe Delo, 8(3) (1962) p. 44-47. (CA 57: 1962).
- CR8 Buck, M. and Stratmann, H. "Determination of Hydrogen Sulfide in the Atmosphere". Staub, 24 (July 1964) p. 241-50. (APCA Abstracts X (8), January 1965).
- CR9 Buck, M. and Geis, H. "Measurement of Hydrogen Sulphide in the Atmosphere. Joint Determination of Hydrogen and Sulfur Dioxide". Staub, Reinhaltung der Luft, 26 (Sept. 1966) p. 379-384. (Fuel Abstracts, 8: 2785, 1967).

MISCELLANEOUS

Other techniques that have been used for H_2S include: polarography (M1, M8, M9), coulometry (M4), x-ray absorption (M2), fluorescence (M3, M7), catalysis (M5), and precipitation (M6). The references are:

- M1 Prchlik J. "Polarographic Methods Applied to Illuminating Gas". Palwa a Voda, 30 (1950) p. 303-8. (CA 45: 5908, 1951).
- M2 Quiram, Ernest R. "New Way to Continuous Hydrogen Sulfide Analysis". Petroleum Refiner, 38(7) (1959) p. 143-4. (CA 53: 1959).
- M3 Wroński, M. "The Use of Mercurated Phenolphthalein and Fluorescein in Chemical Analysis". Zeitschrift fuer Analytische Chemie, 175(6) (1960) p. 432-36. (AA 8: Feb. 1961).
- M4 Ceskoslovenska Akademie Ved. "Electrochemical Gas Analysis". Belg. 624,208, Feb. 14, 1963; Czech. Appl. Oct. 27, 1961; 12 pp. (CA 58: 1963).
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- M6 Demus, H. and Liebert, H. "Analysis of a Mixture of Hydrogen Sulphide, Carbon Dioxide, Carbon Disulphide and Air". Faserforschung und Textiltechnik, 13(8) (1962) p. 376-77. (AA 10: May, 1963).
- M7 Andrew, T.R. and Nichols, P.N.R. "The Determination of Hydrogen Sulfide in the Atmosphere". Analyst, 90(1071) (1965) p. 367-70. (CA 63: 1965).
- M8 Capuano, Italo A. "Continuous Polarographic Analysis for Low Hydrogen Sulfide Concentrations". (to Union Carbide Corp.) U.S. 3,304,243 (Cl.204-1), Feb. 14, 1967. 5 pp.
- M9 Wolf, F. and Langen, H. "Combined Trace Analysis of H_2S and COS in SO_2 -containing Waste Gases". Chemie-Ingenieur-Technik, 39(16) (1967) p. 945-8. (CA 67: 1967).

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